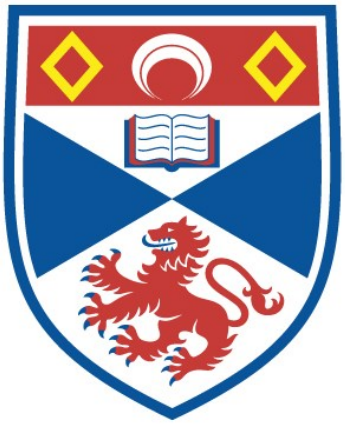
A THEORETICAL METHOD FOR ELECTRONIC STRUCTURE CALCULATIONS ON SYSTEMS OF BIOLOGICAL IMPORTANCE - THE GROUP FUNCTION APPROACH

Donatella Paci

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



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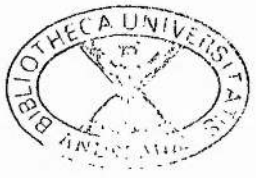

DECLARATIONS

I, Donatella Paci, hereby certify that this thesis has been composed by myself, that it is a record of my own work, and that it has not been accepted in partial or complete fulfilment of any other degree or professional qualification.

Donatella Paci.

I was admitted to the Faculty of Science at the University of St. Andrews under Ordinance General No. 12 on 1st December 1988 and as a candidate for the Degree of Ph.D. on 1st December 1989.

Donatella Paci.

I hereby certify that the candidate has fulfilled the conditions of the Resolution and Regulations appropriate to the Degree of Ph.D.

Colin Thomson.

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I would also like to thank Mum, Dad and Daniele for their support. I dedicate this thesis to them.

ABSTRACT

Theoretical methods for studying molecules of biological importance are reviewed, both *ab initio* and semi-empirical. The Group Function Approach is developed in detail in its strong orthogonal form and corrections to the energy are added for taking into account non-orthogonality effects, depending on the overlaps of the group functions. Approximations are introduced and tested so that this method can be applied to large molecules.

In particular, a system (or a relevant fragment of it) is built up from localized two-electron groups, each one described by a two-electron group function (geminal). Each group function is optimized by using an SCF method with an effective hamiltonian consisting of the two-electron hamiltonian of the group together with the effective potential due to the presence of the other electron groups (and to the external environment, eventually). The wavefunction for the whole molecule is an antisymmetrized product of geminals. The energy is computed as a sum of group contributions. Corrections, depending on up to the second power of the overlaps of two groups at a time, are particularly important in conformational studies. The approximations introduced are based on the consideration that distant groups consisting of two positive and two negative charges see each other as neutral entities and thus do not contribute appreciably in the definition of the effective hamiltonian: the computing effort is greatly reduced in this way, the error introduced is small and can be estimated easily.

The theoretical method presented in this thesis offers a powerful tool for making qualitative predictions of the changes resulting from localized effects, such as twisting around a bond, and it can be usefully applied to conformational studies and geometry optimizations. The other properties which can be calculated are for the most part directly related to the electron density; this determines, for example, the electrostatic potential outside a molecule and hence the position of attack by approaching ions or polar species. Chemical reactions, which involve breaking or re-arrangement of bonds, provide another vast field of application. Such processes usually involve only localized regions in a molecule and the admission of intragroup CI ensures that the study of bond breaking remains valid throughout the whole process.

All necessary computer programmes have been developed and numerical applications have been made to a range of molecules, including hydrocarbons, small molecules containing double bonds and lone pairs, and the amino acid glycine.

A THEORETICAL METHOD FOR ELECTRONIC STRUCTURE CALCULATIONS ON SYSTEMS OF BIOLOGICAL IMPORTANCE – THE GROUP FUNCTION APPROACH –

CONTENTS

PART I

THE THEORETICAL TREATMENT

OF BIOMOLECULAR SYSTEMS

I.1 Introduction.

The theoretical treatment of biomolecular systems is becoming increasingly important in modern science [1,2]. Such theoretical studies allow information to be available that cannot be obtained by experimental methods. Moreover, working hypotheses can be formulated for the experimentalist to test. The aim of this section is to review a number of methods in use for studying large systems, and to introduce the Group Function Approach (developed in details in Part II of this thesis) on which our applications are based.

The study of a chemical system consists in looking for information about its structure and its behaviour in presence of other chemical systems (reactivity). The most useful conceptual framework for the description of chemical structure and reactivity is represented by Potential Energy Surfaces (PES) [2a,3]. A Potential Energy Surface is the mathematical representation of the dependence of the total energy E_{tot} on the nuclear coordinates needed to define the nuclear positions, assumed fixed in space. For a system of M nuclei and N electrons, the total energy is the sum of the kinetic energies of the nuclei $K(\mathbf{x}_n)$ plus the kinetic energies of the electrons $K(\mathbf{x}_e)$ plus the potential energy due to the electrostatic interaction between all the particles (nuclei and electrons), $U(\mathbf{x}_n, \mathbf{x}_e)$,

$$E_{tot} = K(\mathbf{x}_n) + K(\mathbf{x}_e) + U(\mathbf{x}_n, \mathbf{x}_e) \tag{I.1.1}$$

where $\{\mathbf{x}_n\}$ and $\{\mathbf{x}_e\}$ are the sets of nuclear and electronic coordinates respectively.

If we assume that the positions of the nuclei are fixed in space*, the nuclear kinetic energy is negligible and can be dropped from Eq.(I.1.1); the system of N electrons moving in the field of M nuclei has a total energy given by

$$E_{tot} = K(\mathrm{x}_e) + U(\mathrm{x}_n, \mathrm{x}_e) \tag{I.1.2}$$

where $U(\mathrm{x}_n, \mathrm{x}_e)$ depends parametrically on the nuclear coordinates $\{\mathrm{x}_n\}$. The value of E_{tot} in (I.1.2) is unequivocally determined by specifying the nuclear configuration. The nuclear configuration can be specified in terms of either cartesian or internal coordinates. In order to define the latter one has to mention the many experimental evidences for the possibility of extracting through the study of a molecular system some local feature characterizing a smaller system which thus appears as a more or less distorted constitutive unit. In this way the concept of bond was introduced and defined as a constitutive unit localized between two neighbouring atoms. Internal coordinates are given by bond lengths, bond angles and dihedral (or torsional) angles. A bond length is the distance between two neighbouring atoms forming a bond, a bond angle is the angle between two bonds with an atom in common and a dihedral angle is the angle between the planes formed by two pairs of bonds having a bond in common. If M nuclei are present, 3M-6 coordinates are needed in a polyatomic molecule to define the nuclear configuration (3M-5 in a linear molecule). Therefore for a system of M nuclei the Potential Energy Surface has 3M-5 dimensions (3M-4 if the molecular system is linear), since to the dimensions for nuclear coordinates

* This is Born-Oppenheimer approximation, based on the fact that the masses of the nuclei are much greater than the masses of the electrons (a proton or a neutron are about 2000 times heavier than an electron); this implies that the motions of the electrons are not affected by the slow movements of the nuclei; the equilibrium configuration can be assumed as a fixed configuration for the nuclei, particularly when the mean distance covered by a nucleus in its vibration around an equilibrium position is small with respect to the molecular size; this is the supposition we will make from now on.

must be added the dimension that measures the energy. The PES contain a large amount of information about chemical structure and reactivity. Its minima represent (meta)stable nuclear configurations (conformations); its maxima and inflection points should be associated with unstable states and it is possible to study the response to perturbation (reactivity) moving away over the surface from a minimum. In fact a chemical reaction can be thought of as the changes a molecule is subjected to when a perturbation occurs. Such perturbation can be due to the presence of another molecule or another part of the same molecule or to an external field. The structure of the molecule in question, originally in one of its stable configurations, reactant (represented by a minimum in a PES), changes continuously; it first assumes increasing values of energy, up to a maximum of energy corresponding to the so called transition state (represented by a saddle point on the PES) and then decreasing values of energy down to a new stable configuration (reaction product). In particular, it is possible to evaluate a rotational barrier in a molecule. One speaks about internal rotation if some of the dihedral angles are changed while other internal coordinates remain unaffected. When a (part of a) PES is determined as function of certain selected dihedral angles, the energy difference between a neighbouring minimum and maximum is called the barrier to the corresponding rotation. The whole PES is usually not known; only a part of it is studied. Many theoretical methods are commonly applied to calculate the energy values. In any case, a series of energy values are calculated corresponding to a particularly interesting structure and change; it is common practice to use minimization methods for finding equilibrium structures.

The total energy of a molecule is expressible in terms of bond contributions ϵ_i, bond-bond interactions ϵ_{ij}, and so on. This conclusion follows from the analysis of a great number of experimental results and leads to a so-called empirical bond systematic [4],

$$E_{tot} = \sum_{i}^{bonds} \epsilon_i + \sum_{i}^{bonds} \sum_{j<i}^{bonds} \epsilon_{ij} + \sum_{i}^{bonds} \sum_{j<i}^{bonds} \sum_{k<j}^{bonds} \epsilon_{ijk} + \ldots$$

where the quantities $\epsilon_i, \epsilon_{ij}, \ldots$ do not depend on the environment. The very old empirical systematics for the heat of formation of a molecule are examples of numerical systematics. Good results are obtained also if the calculation is restricted to two-body interactions ϵ_{ij} between adjacent and vicinal bonds. Analytical systematics are also possible. They constitute the basis for empirical energy calculations which will be discussed later. We will see that other molecular properties are expressible in terms of bond contributions. An enormous body of experimental data can be interpreted by bond additivity rules and sometimes by relatively small deviations which in turn can be referred to special effects. Indeed one can identify characteristic bond distances, bond angles, force constants, stretching frequencies, indirect spin-spin coupling constants, etc.

For a given system many interesting properties can be calculated by theoretical methods. They all are related to the changes in the electronic situation of the system, sometimes not affecting the nuclear configuration.

Electric properties are related to the charge distribution $\rho(\mathbf{r})$ (charge density),

$$\rho(\mathbf{r}) = -\rho_e(\mathbf{r}) + \sum_A Z_A \delta(\mathbf{r} - \mathbf{r}_A) \qquad \text{(I.1.3)}$$

where $\rho_e(\mathbf{r})$ is the electronic distribution; Z_A is the atomic number, $\mathbf{r}_A$ is the position of nucleus A, and

$$\delta(\mathbf{r} - \mathbf{r}_A) = \begin{cases} 1 & \text{for } \mathbf{r}=\mathbf{r}_A, \\ 0 & \text{otherwise.} \end{cases}$$

is the Dirac delta function.

Integration of $\rho_e(\mathbf{r})$ over the whole space obviously gives the total number of electrons (N) in the molecule,

$$\int \rho_e(\mathbf{r}) dV = N.$$

The information contained in $\rho_e(\mathbf{r})$ can be very useful, for instance in making predictions on charge-controlled chemical reactions. One is often interested in the influence of different atoms in the molecule and thus it is useful to approximate the charge distribution in terms of point charges associated with the atoms from which the molecule is built up. In this manner the concept of atomic charge can be introduced. The atomic charge is not a physical quantity. It can have many different theoretical definitions, reflecting the ambiguity of the concept. A conceptually simple definition is based on the division of the whole space into domains, one for each atom [5]. The atomic charge q_A is then defined as

$$q_A = Z_A - \int_{V_A} \rho_e(\mathbf{r}) dV \tag{I.1.4}$$

where V_A is the domain containing atom A. It is not always easy to find an appropriate division of space and the integrals in (I.1.4) are rather difficult to evaluate.

Charge distributions can also be described in terms of multipoles. The potential energy E of the charge distribution $\rho_e(\mathbf{r})$ in an external field $V_{ext}(\mathbf{r})$ is

$$E = \int \rho_e(\mathbf{r}) V_{ext}(\mathbf{r}) dV.$$

By expanding $V_{ext}(\mathbf{r})$ in a Taylor series, we have

$$E = QV_{ext}(\mathbf{0}) + \sum_i \mu_i \frac{\partial V_{ext}}{\partial r_i}|_0 + \frac{1}{3} \sum_{i,k} Q_{ik} \frac{\partial^2 V_{ext}}{\partial r_i \partial r_k}|_0 + \ldots$$

where Q is the total charge of the system, and r_i is x, y or z according to i=1, 2 or 3. The dipole moment has components μ_i given by

$$\mu_i = \int \rho_e(\mathbf{r}) r_i dV$$

while the quadrupole moment Q_{ik} is defined in terms of its tensor components

$$Q_{ik} = \frac{3}{2} \int \rho_e(\mathbf{r})[r_i r_k - \frac{1}{3}\delta_{ik} r^2] dV.$$

Similarly, higher multipole moments can be defined. Total dipole moments can also be estimated as vectorial sums of transferable bond contributions to a surprisingly good accuracy.

A very informative picture of molecular electrostatics emerges from an internal transform of the molecule charge distribution, the Molecular Electrostatic Potential (MEP). The MEP $V(\mathbf{r})$ that is created in the space around a molecule by its electrons and nuclei is given by

$$V(\mathbf{r}) = \int \frac{-\rho_e(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \sum_m \frac{Z_m}{|\mathbf{R}_m - \mathbf{r}|} \qquad \text{(I.1.5)}$$

where $-\rho_e(\mathbf{r}')$ is the electronic charge density and Z_m and $\mathbf{R}_m$ are the charge and position vector of the m-th nucleus. $V(\mathbf{r})$ may be regarded as the potential of the molecule for interaction with an electric charge located at the point $\mathbf{r}$. Thus a positive charge is attracted to those regions in which $V(\mathbf{r})$ is negative since this leads to a negative stabilizing interaction energy, and it is repelled from regions of positive potential in which the interaction energy is destabilizing.

The accuracy of information obtained from a calculation is strictly dependent on the definition of a model for the system. This model is quite simple for small systems in the gas phase and it contains only those nuclei and electrons which directly participate in the process. In the modelling of a biomolecular structure or process the solvent must be included and a distinction must be made between two broad classes. In the first, practically all atoms of the system contribute to the property or take part in the change, and therefore an overall treatment is necessary; empirical energy calculations can be applied with some success. In other cases, changes are localized to a relatively small part, the relevant fragment. A number of quantum mechanical methods has been used for studying the latter. The prototype approach is usually used, where broken bonds at the frontiers of the fragment are saturated by some appropriately

selected atoms: hydrogen atoms or "pseudoatoms" which mimic the usually polyvalent atom which has been cut off [2]. Large systems are often built up from relatively simple building blocks. One such building block is the relevant fragment. Its environment can be divided into different regions. The accuracy of description of the other building blocks decreases with the distance from the chemically interesting fragment.

I.2 Empirical Energy Calculations.

Empirical methods are based on the observation that bond properties are more or less transferable within certain classes of molecules. Regions of potential energy surfaces around their local minima can be approximated by a sum of simple analytical expressions with constants that are fitted to reproduce a great number of experimental quantities as closely as possible [1,2b].

In the empirical approach, the total energy of a molecular system is approximated as

$$E_{tot} = E_b + E_t + E_{nb} \tag{I.2.1}$$

where E_b, E_t, E_{nb} stand for bonding, torsional and non bonding interactions respectively.

Bonding interactions are approximated by a sum of stretching, bending and cross terms

$$E_b = \sum_i E_i(r_0) + \frac{1}{2}\sum_r k_r(r - r_0)^2 + \frac{1}{2}\sum_\theta k_\theta(\theta - \theta_0)^2 + cross\ terms \tag{I.2.2}$$

where $E_i(r_0)$ is a bond energy in the standard geometry, r, r_0, θ, θ_0 denote actual and equilibrium bond lengths and angles, respectively, determined mainly from the molecular geometry, while k_r and k_θ stand for quadratic force constants, derived from relatively high-frequency vibrations. The summation extends over all stretching and

bending degrees of freedom. *Cross terms*, if considered, include stretch-stretch, bend-bend or bend-stretch contributions. In general, these simple quadratic potentials are used, though more realistic Morse potentials can be applied with little increase in complexity.

The general form of the torsional potential which accounts for the hindered rotations around bonds is

$$E_t = \frac{1}{2}\sum V_\phi^m[1-\cos(m\phi+\delta)] \tag{I.2.3}$$

where V_ϕ^m is the m-fold rotational barrier and δ is the phase. The barrier height is derived from the rates of isomerization of molecules while m and δ are determined from symmetry considerations.

The non bonding term is usually expressed in the following general form

$$E_{nb} = \epsilon^{-1}\sum q_i q_j r_{ij}^{-1} + \sum V_{Hb}(d_{ij}) + \sum C_{ij}[(r_{ij}^*)^n - \frac{n}{6}(r_{ij}^*)^6] \tag{I.2.4}$$

The first term corresponds to electrostatic interactions between atom i and j, bearing net charges of q_i and q_j; ϵ is the dielectric constant. The second term is the Hydrogen bonding potential. Van der Waals interactions are accounted for in the last term, where $r_{ij}^* = \frac{r_{ij}^0}{r_{ij}}$, C_{ij} and r_{ij}^0 are adjustable parameters, differing for various types of atomic pairs. In most cases n is equal to 12.

Several approaches are proposed which differ mainly in the parametrization.

The atomic net charges q_i are calculated by quantum mechanical methods or derived together with the Van der Waals parameters from the observed geometry of molecular crystals or fitted to quantum-mechanically calculated electrostatic potentials.

$$V_{Hb}(d_{ij}) = A_{ij}d_{ij}^{-12} - B_{ij}d_{ij}^{-10} \tag{I.2.5}$$

where A_{ij}, B_{ij} are adjustable parameters.

For example, for amide-carbonyl hydrogen bonds:

$$V_{Hb}(d_{ij}) = A_{ij}d_{ij}^{-12} - B_{ij}d_{ij}^{-6}e^{-\theta^2\sigma^2} + A'_{ij}d_{ij}^{-12} - B'_{ij}d_{ij}^{-6}(1 - e^{-\theta^2\sigma^2})$$

where A_{ij}, B_{ij} are for Hydrogen bonding interactions, A'_{ij}, B'_{ij} for Van der Waals interactions, d_{ij} is the $O - H$ separation, θ is the $H - N - O$ angle and σ is an adjustable parameter.

In spite of its simple algebraic form, the empirical function in Eq. (I.2.1) may yield good results if the parameters are carefully chosen using calculations on small molecules. The calculated properties range from equilibrium molecular geometries and conformations to vibrational spectra, crystal packing geometries, strain energies. Agreement between experiment and calculations is within approximately 20 pm for geometries, 4 kJ/mol for strain energies and 30 cm^{-1} for vibrational frequencies. Empirical energy expressions are valid however only for the neighbourhood of local minima on the potential energy surface. Consequently bond breaking or formation cannot be treated.

I.3 Quantum Chemical Methods Applied to the Study of Large Molecules of Biological Importance.

The proper description of the electronic structure of extended systems by state-of-the-art methods remain a challenging task of quantum chemistry. These large systems are always built up from relatively simple building blocks. The existence of such building blocks or fragments is a fundamental principle in experimental physical chemistry [6]. The Group Function Theory provides a theoretical framework for the quantum mechanical treatment of this situation. It will be extensively discussed in the second part of this thesis.

Generally, those atoms directly involved in the chemical process are treated quantum mechanically (relevant fragment) and the remainder (for example the solvent, or parts of the molecule far from the relevant fragment) are treated as classical systems [2b]. More precisely, the system can be formally divided into subsystems, one of such subsystems being the relevant fragment; the accuracy and the level of description of each subsystem decreases with the distance from the chemically interesting fragment. The total energy of the system is the sum of the energies of the subsystems plus their interactions.

Quantum chemical methods are based on the Schrödinger equation (see I.3.1) from which a wavefunction is obtained, containing all the information needed to describe the properties of the system of particles. An exact solution of the Schrödinger equation is possible only in a few very simple cases. Approximate solutions can be obtained at different levels of accuracy depending on the models accepted for the

description of the system. If adjustable parameters and empirical quantities are introduced in the quantum mechanical calculation, the so-called semi-empirical methods are obtained.

I.3.1 *AB INITIO* methods.

I.3.1.1 The Schödinger Equation.

The electronic structure and properties of any molecule may be determined in principle from the complex function Ψ, which is a solution of Schödinger's (time-independent) equation [7]. For a system of N electrons this equation takes the form,

$$\hat{H}\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) = E\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N) \qquad \text{(I.3.1.1)}$$

where $\mathbf{x}_i$ symbolizes all the variables needed in referring to electron i,

$\mathbf{x}_i = (x_i, y_i, z_i, s_i)$,

x_i, y_i, z_i spatial variables, s_i spin variable (see APPENDIX A);

$\hat{H}$ is the Hamiltonian operator, associated with the observable energy, following from quantum mechanical principle, in a.u., *

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* Atomic units (a.u.) are employed. In a.u., $e = 1.6021 \times 10^{-19} C$ the charge of a proton, $\hbar = 1.0545 \times 10^{-34} Js$ measuring action, $m = 9.1091 \times 10^{-31} kg$, the mass of the electron and $\chi_0 = 4\pi\epsilon_0, \epsilon_0 = 8.8542 \times 10^{-12} Fm^{-1}$ being the permittivity of free space, all take unit values and may be dropped from all equations provided the symbols occurring are reinterpreted as the numerical (i.e. dimensionless) measure of the quantities they represent. Strictly speaking, these are quantities, not units. The term "unit" is nevertheless adopted, in conformity with everyday usage. In practice it is convenient to introduce the "bohr", $a_0 = (\hbar^2\chi_0)/(me^2) = 5.2916 \times 10^{-11} m$, and the "Hartree", $E_h = (me^4)/(\chi_0^2\hbar^2) = 4.3594 \times 10^{-18} J = 27.211 eV$, and to express other quantities in terms of the most convenient combinations of $e, \hbar, m, a_0$ and E_h.

$$\hat{H} = \sum_{i=1}^{N} h(i) + \frac{1}{2} \sum_{i,j=1}^{N} {}' g(i,j) \qquad \text{(I.3.1.1}a\text{)}$$

$$h(i) = -\frac{1}{2}\nabla^2(i) + V(i) \qquad \text{(I.3.1.1}b\text{)}$$

$$\nabla^2(i) = \left(\frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}\right) \qquad \text{(I.3.1.1}c\text{)}$$

$-\frac{1}{2}\nabla^2(i)$ is the kinetic energy operator of electron i;

$V(i) = -\sum_n \frac{Z_n}{r_{ni}}$ is the potential energy of electron i in the field of the nuclei which are assumed fixed in space (Born-Oppenheimer approximation), r_{ni} being the magnitude of the position vector of electron i relative to nucleus n, and Z_n the charge of nucleus n;

$g(i,j) = \frac{1}{r_{ij}}$ is the electrostatic repulsion of electrons i and j, r_{ij} being the separation between electrons i and j;

The function Ψ, called the wavefunction, describes the state of the N-electron system in the sense that $|\Psi|^2 d\tau$ can be interpreted as being the probability of finding electrons $1, 2, ..., N$ in (space-spin) volume elements $dx_1, dx_2, ..., dx_N$ respectively ($d\tau = dx_1 dx_2 ... dx_N$), provided Ψ is normalized, that is to say, $\int |\Psi^2| d\tau = 1$.

Given this physical meaning of the wavefunction it follows that it must be continuous, single-valued and quadratically integrable; this implies that not every solution of the Schrödinger equation is acceptable. Besides, Pauli's Principle states that the wavefunction must be antisymmetric.

Eq. (I.3.1) is an eigenvalue equation and possesses solution with the above characteristics only for certain values of the eigenvalue E. The set of all acceptable solutions describes the so called stationary states of the system; for each of them the electron distribution in the molecule can be calculated. The mean ('expectation') value of any physical observable can also be computed, using the formula

$$< A >= \int_{\mathbf{x}_1'=\mathbf{x}_1} \hat{A}\rho_1(\mathbf{x}_1, \mathbf{x}_1')d\tau \qquad \text{(I.3.1.2)}$$

Here $\hat{A}$ is the quantum mechanical (hermitian) operator * associated with the observable A; it works on functions of $\mathbf{x}_1$ only. We will put $\mathbf{x}_1' = \mathbf{x}_1$ after operating with $\hat{A}$ but before completing the integration

$$\rho_1(\mathbf{x}_1; \mathbf{x}_1') = N \int \Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)\Psi^*(\mathbf{x}_1', \mathbf{x}_2, ..., \mathbf{x}_N)d\mathbf{x}_2...d\mathbf{x}_N \qquad \text{(I.3.1.2}a\text{)}$$

is a generalized one-particle density function (the one-particle density matrix). In particular the diagonal element $\rho_1(\mathbf{x}_1) = \rho_1(\mathbf{x}_1; \mathbf{x}_1)$ is the probability of finding any of the N electrons in $d\mathbf{x}_1$, independently of the positions of other electrons. The ordinary electron density function measured by X-ray crystallographers, defining the electronic distribution in space (ρ_e in (I.1.3)), is obtained by integrating $\rho_1(\mathbf{x}_1)$ over spin, $P_1(\mathbf{r}_1) = \int \rho_1(\mathbf{x}_1)ds_1$. A two-particle density matrix can be defined in the same way,

$$\rho_2(\mathbf{x}_1, \mathbf{x}_2; \mathbf{x}_1', \mathbf{x}_2') = N(N-1) \int \Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N)\Psi^*(\mathbf{x}_1', \mathbf{x}_2', ..., \mathbf{x}_N)d\mathbf{x}_3...d\mathbf{x}_N. \qquad \text{(I.3.1.2}b\text{)}$$

The energy E, in Born-Oppenheimer approximation, is the energy of the N electrons moving in the field provided by the nuclei. E assumes a set of values, corresponding to various electronic states. The total energy of the molecule, E_{tot}, is obtained by adding the nuclear-nuclear repulsion energy to the electronic energy:

* An hermitian operator $\hat{A}$ is defined from $\int \phi_i^*(\hat{A}\phi_j)d\tau = \int(\hat{A}\phi_i)^*\phi_j d\tau$. It has real eigenvalues and orthogonal eigenfunctions, i.e. $\int \phi_i^*\phi_j d\tau = 0$ if $i \neq j$.

A quantum mechanical operator associated with a physical observable must be hermitian because its eigenvalues correspond to the values obtained from measurements of the observable itself.

$$E_{tot} = E + \sum_{A<B} \frac{Z_A Z_B}{R_{AB}} \qquad \text{(I.3.1.3)}$$

R_{AB} being the distance between nuclei A and B. E depends parametrically on the nuclear coordinates. It represents an effective Potential Energy for the nuclei, in the Born-Oppenheimer approximation. In this case the wavefunction for the whole system (nuclei and electrons) can be written as a product $\Psi_v^0 = \Phi_v^0(\mathbf{x}_n)\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_N, R_0)$, where Ψ represents the electronic part of the system in one of its stationary states; it depends on the equilibrium nuclear configuration R_0. $\Phi_v^0(\mathbf{x}_n)$ is a member of a set of nuclear wavefunctions obtained by solving the equation

$$[K(\mathbf{x}_n) + E_{tot}]\Phi_v^0(\mathbf{x}_n) = E_v^0 \Phi_v^0(\mathbf{x}_n),$$

one such equation for any electronic configuration. In other words, E_{tot} is used for defining points of the Potential Energy Surfaces for the given nuclear configuration, one for each electronic state.

I.3.1.2 The Independent Particle Model. The Hartree-Fock Theory.

Up to now the essential principles of quantum chemistry have been summarized. They are the foundation of theoretical methods and approximations used for describing atoms and molecules and the processes they are subjected to and constitute the remote background of the applications of the Group Function approach we will develop in the second part of this thesis, but they cannot be employed in calculations on systems of great complexity without introducing approximations. In fact the Schrödinger equation is exactly solvable only in a few cases. For the Hydrogen atom, for example, one finds one-electron wavefunctions, called atomic spin-orbitals (SO's) (see APPENDIX A).

It is not so easy to solve for more complex atoms or for molecules because it is very difficult to take into account the electronic interactions. Approximate methods have to be tried. If electrons were non-interacting the hamiltonian would be a sum of

one-electron hamiltonians $\hat{H} = \sum_i h(i)$ and the corresponding wavefunction could be taken as a product of one-electron eigenfunction, (atomic or molecular spin orbitals) one factor for each electron,

$$\Psi = \psi_1(\mathrm{x}_1)\psi_2(\mathrm{x}_2)...\psi_N(\mathrm{x}_N).$$

In this case we could easily obtain an exact solution by using the method of separation of variables and by solving a one-electron eigenvalue equation; this is the so-called Independent Particle Model (IPM). Products of this kind are eigenfunctions of the hermitian operator h and therefore they form a complete set according to the postulates of quantum mechanics. Thus it is possible to describe the wavefunction Ψ of a many-electron atom or molecule as a linear combination of antisymmetrized products.

An antisymmetrized product of one-electron functions can be constructed as a determinant built up from one-electron SO's $\{\psi_i\}$, each one 'occupied' by an electron, i.e., describing one electron,

$$det \begin{pmatrix} \psi_1(\mathrm{x}_1) & \psi_1(\mathrm{x}_2) & \dots & \psi_1(\mathrm{x}_N) \\ \psi_2(\mathrm{x}_1) & \psi_2(\mathrm{x}_2) & \dots & \psi_2(\mathrm{x}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\mathrm{x}_1) & \psi_N(\mathrm{x}_2) & \dots & \psi_N(\mathrm{x}_N) \end{pmatrix} \qquad \text{(I.3.1.4}a\text{)}$$

The determinantal wavefunction (Slater determinant) is often written in the shorthand notation, $|\psi_1\psi_2...\psi_N|$ [8] and it is equivalent to the antisymmetrized product

$$\hat{A}[\psi_1(\mathrm{x}_1)\psi_2(\mathrm{x}_2)\dots\psi_N(\mathrm{x}_N)] \qquad \text{(I.3.1.4}b\text{)}$$

where

$$\hat{A} = \sum_P \epsilon_P P, \qquad \text{(I.3.1.4}c\text{)}$$

P being any permutation which exchanges variables and $\epsilon_P = 1$ for an even number of transpositions and $\epsilon_P = -1$ if an odd number of transpositions occurs in P.

The Hartree-Fock method [9] uses these principles. The total many-electron wavefunction is written in the form of a single determinant of normalized and orthogonal SO's.

I.3.1.3 The Variation Method.

Now we consider the problem of optimizing the SO's in the one-determinant wavefunction. A fundamental theorem states that the energy, calculated by minimizing the functional

$$E[\Phi] = \frac{<\Phi|\hat{H}|\Phi>}{<\Phi|\Phi>} \qquad \text{(I.3.1.5)}$$

obtained from the energy expectation value formula $E[\Psi] = \frac{<\Psi|\hat{H}|\Psi>}{<\Psi|\Psi>}$ on replacing the exact wavefunction Ψ with an approximate one containing variable parameters, provides an upper bound to the true energy (variational principle).

A system in its ground state is usually well described by a single determinant of doubly occupied orbitals (closed-shell ground state); this means that the set of SO's used for the determinant (occupied SO's) consists of pairs of SO's, the two orbitals of the pair differing only in the spin factor. We employ Slater rules [8] to derive the explicit form of (I.3.1.4) in the case of a normalized one-determinant wavefunction. The result is

$$E = \sum_i <\phi_i|h|\phi_i> + \frac{1}{2}\sum_{i,j} <\phi_i\phi_j||\phi_i\phi_j> \qquad \text{(I.3.1.6)}$$

where the summations run over the occupied spin-orbitals and we have introduced the "antisymmetrized 2-electron integral"

$$<\phi_i\phi_j||\phi_i\phi_j> = <\phi_i\phi_j|g|\phi_i\phi_j> - <\phi_i\phi_j|g|\phi_j\phi_i>$$

The Dirac notation for the integrals is standard:

$$< \phi_i|h|\phi_j >= \int \phi_i^*(\mathbf{x}_1)h(1)\phi_j(\mathbf{x}_1)d\mathbf{x}_1$$

$$< \phi_i\phi_k|g|\phi_j\phi_l >= \int \phi_i^*(\mathbf{x}_1)\phi_k^*(\mathbf{x}_2)\phi_j(\mathbf{x}_1)\phi_l(\mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2$$

To obtain a stationary value, we let $\phi_k \rightarrow \phi_k + \delta o_k$ and set $\delta E = 0$ (to first order) for all $\delta\phi_k$, remembering that (I.3.1.6) remains valid only when the spin-orbitals remain normalized and orthogonal. With the change δo_k, we obtain a corresponding first order variation of the energy

$$\delta E^{(k)} =< \delta\phi_k|h|\phi_k > +c.c. + \frac{1}{2}(\sum_j < \delta\phi_k\phi_j||\phi_k\phi_j > + \sum_i < \phi_i\delta\phi_k||\phi_i\phi_k >) + c.c.$$

where each c.c. is the complex conjugate of the preceding term. The two sums in the parentheses, however, are identical, because the integrals are invariant against exchange of the indices on both sides of the ||, simultaneously, while the name of the summation index (i or j) is immaterial. Thus

$$\delta E^{(k)} = (< \delta\phi_k|h|\phi_k > + \sum_i < \delta\phi_k\phi_i||o_k\phi_i >) + c.c.$$

The resultant first order change δE is $\delta E = \sum_k \delta E^{(k)}$.

It is usual to introduce two new operators J_i and K_i, defined as follows,

$$J_i(1)\phi(\mathbf{x}_1) = [\int g(1,2)\phi_i(\mathbf{x}_2)\phi_i^*(\mathbf{x}_2)d\mathbf{x}_2]\phi(\mathbf{x}_1)$$

$$K_i(1)\phi(\mathbf{x}_1) = [\int g(1,2)\phi_i(\mathbf{x}_1)\phi_i^*(\mathbf{x}_2)o(\mathbf{x}_2)d\mathbf{x}_2]$$

J_i is the coulomb operator associated with an electron in ϕ_i working on an arbitrary function ϕ; in other words, $\phi(\mathbf{x}_1)$, is simply multiplied by the potential

energy of an electron at $\mathbf{x}_1$ in the field due to a charge distribution $|\phi_i(\mathbf{x}_2)|^2$ (in electrons per unit volume). K_i is the exchange operator.

It is also convenient to introduce the total coulomb and exchange operators, $J = \sum_i J_i$ and $K = \sum_i K_i$, where the summation is over all occupied SO's.

From these definitions of J and K, it follows that the two-electron term in the energy expectation value (I.3.1.6) can be expressed in terms of expectation values of a one-electron operator, thus

$$\sum_{i,j} < \phi_i\phi_j||\phi_i\phi_j >= \sum_j < \phi_i|J_j|\phi_i > - \sum_j < \phi_i|K_j|\phi_i >=$$

$$=< \phi_i|J - K|\phi_i >=< \phi_i|G|\phi_i >$$

where $G = J - K$.

The energy expression can be written as

$$E = \sum_i^{occ.spinorbs} < \phi_i|h + \tfrac{1}{2}G|\phi_i >$$

For a closed-shell system, after spin integration

$$E = \sum_i^{occ.spac.orbs} 2 < \varphi_i|h + 2J - K|\varphi_i >= \sum_i 2(h_{ii} + 2J_{ii} - K_{ii})$$

where φ_i is now the orbital factor of the spin-orbital and

$$\varphi_l(\mathbf{r})\alpha = \phi_{2l-1}(\mathbf{x})$$

$$\varphi_l(\mathbf{r})\beta = \phi_{2l}(\mathbf{x})$$

$$h_{ii} =< \varphi_i|h|\varphi_i >$$

$$J_{ii} =< \varphi_i|J|\varphi_i >$$

$$K_{ii} =< \varphi_i|K|\varphi_i >$$

From now on the derivation will employ spatial orbitals φ_i.

Defining the Fock hamiltonian operator $F = h + G$, it results

$$\delta E^{(k)} =< \delta\varphi_k|F|\varphi_k > + < \varphi_k|F|\delta\varphi_k >= 0$$

Since this $\delta E^{(k)}$ evidently gives the first order variation of a 1-electron energy expectation value $\epsilon_k =< \varphi_k|F|\varphi_k >$, the Fock operator may be regarded as the effective hamiltonian for a single electron moving in the field of the nuclei (contained in h) together with an effective "coulomb-exchange" field representing the presence of all other electrons.

The requirement that $\delta E^{(k)}$ be stationary strongly suggests that the orbital energies ϵ_k might be eigenvalues of F, but to verify this conjecture we must take proper account of the orthogonality constraints,

$$< \varphi_j|\varphi_k >= \delta_{jk}$$

where

$$\delta_{jk} = \begin{cases} 1 & \text{if j=k,} \\ 0 & \text{otherwise.} \end{cases}$$

The new SO's $\varphi_k + \delta\varphi_k$ must satisfy these condition, i.e. $\delta\varphi_k$ must be orthogonal to φ_k for preserving normalization and to every φ_j with $j \neq 0$ for ensuring orthonormality in the new set of orbitals,

$$< \delta\varphi_k|\varphi_k > + < \varphi_k|\delta\varphi_k >= 0$$

$$< \delta\varphi_k|\varphi_j >= 0; \; < \varphi_j|\delta\varphi_k >= 0; \; j \neq k$$

These constraints may be combined with $\delta E^{(k)} = 0$ by using the mathematical method of Lagrangian multipliers

$$< \delta\varphi_k|F|\varphi_k > - \sum_j \epsilon_{jk} < \delta\varphi_k|\varphi_j >= 0$$

$$< \varphi_k|F|\delta\varphi_k > - \sum_j \epsilon_{kj} < \varphi_j|\delta\varphi_k >= 0$$

where $\epsilon_{jk}, \epsilon_{kj}$ are arbitrary constants.

Since F is hermitian,

$$(\epsilon_{jk} - \epsilon^*_{kj}) < \delta\varphi_k|\varphi_j >= 0 \quad \forall j,k$$

Thus

$$\epsilon_{jk} = \epsilon^*_{kj}$$

and

$$F\varphi_k - \sum_j \epsilon_{jk}\varphi_j = 0 \quad \forall k$$

or, in matrix notation,

$$F\Phi = \Phi\epsilon$$

where $\Phi = (\varphi_1, \varphi_2, ...)$ and ϵ is a square matrix with elements having arbitrary values. A one-determinant wavefunction is invariant under unitary mixing of the orbitals; new orbitals $\bar{\Phi} = \Phi\mathbf{U}$ may be introduced; and then

$$F\bar{\Phi} = \bar{\Phi}(\mathbf{U}^\dagger\epsilon\mathbf{U}) = \bar{\Phi}\bar{\epsilon}$$

Thus, without changing the many electron wavefunction itself, we may always change the orbitals so that a diagonal $\bar{\epsilon}$ is obtained. Dropping the bars,

$$F\Phi = \Phi\epsilon$$

In other words, every orbital satisfies $F\varphi_i = \epsilon\varphi_i$ and it is then an eigenfunction of an one-electron eigenvalue equation. Since F depends on Φ through the electron interaction terms, the eigenvalue equation must be solved iteratively. This is the Self Consistent Field (SCF) method for solving an Hartree Fock equation.

Every time an eigenvalue equation has to be solved where the definition of the operator is dependent on the form of the wavefunctions to be optimized a SCF method can be employed. This is the case, for example, of the Group Function Method; following from the direct application of the variational theorem to a variational wavefunction defined as an antisymmetrized product of (antisymmetric) group wavefunctions, an eigenvalue equation remains to be solved for each electron group, having an effective hamiltonian defined as a function of the wavefunctions of the other groups and describing the effective field they generate around the electrons of the group in question. A great number of theoretical procedures are in fact applications of the SCF method.

Reasonable first approximations to the atomic orbitals for heavier atoms are hydrogen-like orbitals, obtained from the Hydrogen orbitals by substituting their exponents with variable parameters. Linear combinations of Slater orbitals or gaussian orbitals are often used to reproduce atomic orbitals (see APPENDIX A). The SCF method has been extensively applied to calculations on molecules too after the introduction of the Roothaan LCAO (Linear Combination of Atomic Orbitals) approximation for describing one-electron molecular wavefunctions (Molecular Orbitals, MOs) [10].

In general it is always possible to expand each φ_i as a linear combination of arbitrary basis functions $\chi = (\chi_1, \chi_2, ..., \chi_m)$,

$$\varphi_i = \sum_j \chi_j T_{ji} = \chi \mathbf{T}$$

$F\Phi = \Phi\epsilon$ becomes, for a closed-shell system,

$$\mathbf{FT} = \epsilon \mathbf{ST}$$

where

$F_{\mu\nu} = h_{\mu\nu} + G_{\mu\nu}$

$S_{\mu\nu} =< \chi_\mu | \chi_\nu >$

$h_{\mu\nu} =< \chi_\mu | h | \chi_\nu >$

$G_{\mu\nu} = \sum_{\lambda,\sigma} P_{\sigma\lambda}[(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\sigma|\lambda\nu)]$;

$(\mu\nu|\lambda\sigma) =< \mu\lambda|g|\nu\sigma >$

$P_{\sigma\lambda} = 2\sum_j^{occ} T_{\sigma j} T^*_{\lambda j}$

I.3.1.4 The Electron Density.

Atomic and molecular states can be described generally by using linear combinations of determinants of spin-orbitals, the Hartree-Fock wavefunction being simply a one-determinant approximation. Since each term is defined by stating a "configuration" of occupied SO's, this expansion procedure is often referred to as the method of "Configuration Interaction" (CI). For a state described by a Ψ which is a linear combination of Slater determinants the density function can be expanded in the form

$$\rho(\mathbf{x}_1; \mathbf{x}'_1) = \sum_{R,S} \rho_{RS} \psi_R(\mathbf{x}_1) \psi^*_S(\mathbf{x}'_1) \qquad \text{(I.3.1.7}a\text{)}$$

where ρ_{RS} are numerical coefficients and the spin orbitals ψ_R and ψ^*_S arise from Ψ and Ψ^* respectively.

The one-electron energy becomes,

$$< \sum_i h(i) >= \sum_{R,S} \rho_{RS} < \psi_S|h|\psi_R > .$$

The required ρ_{RS} is thus simply the coefficient of $< \psi_S|h|\psi_R >$ in the usual orbital expression for the one-electron energy. The density matrix without reference to spin is similarly

$$P(\mathbf{r}_1;\mathbf{r}'_1) = \sum_{R,S} P_{RS}\varphi_R(\mathbf{r}_1)\varphi^*_S(\mathbf{r}'_1) \qquad \text{(I.3.1.7}b\text{)}$$

where P_{RS} is a numerical coefficient obtained as the result of spin integration. If we express each one-electron function as a linear combination of arbitrary basis functions $\chi = (\chi_1, \chi_2, ..., \chi_m)$, then $\varphi_R(\mathbf{r}_1) = \sum_i \chi_i(\mathbf{r}_1)T_{iR}$ and the electron density takes the general appearance

$$P(\mathbf{r}_1) = P(\mathbf{r}_1;\mathbf{r}_1) = \sum_{i,j} P^{\chi}_{ij}\chi_i(\mathbf{r}_1)\chi_j(\mathbf{r}_1)$$

$$P^{\chi}_{ij} = \sum_{R,S} P_{RS}T_{iR}T^*_{jS}$$

For a closed-shell system $P_{RS} = 2\delta_{RS}$ and P^{χ}_{ij} becomes $P_{\sigma\lambda}$ as defined in the previous section.

When the basis consists of orbitals (e.g. AO's) with a well-defined localization in space the coefficients permit a quantitative analysis of the form of the electron distribution. We define normalized orbitals and overlap densities (assuming for convenience real orbitals)

$d_i(\mathbf{r}) = \chi_i(\mathbf{r})^2$, orbital density,

$d_{ij}(\mathbf{r}) = \chi_i(\mathbf{r})\chi_j(\mathbf{r})/S_{ij}$, overlap density, with $S_{ij} =< \chi_i(\mathbf{r})|\chi_j(\mathbf{r}) >$, and find

$$P(\mathbf{r}) = \sum_i q_i d_i(\mathbf{r}) + \sum_{i<j} q_{ij} d_{ij}(\mathbf{r}) \qquad \text{(I.3.1.8)}$$

where $q_i = P_{ii}$, $q_{ij} = 2S_{ij}Pij$, $(i \neq j)$.

Since integration of $P(\mathbf{r})$ over all space must yield N (the number of electrons) it follows that

$$\int P(\mathbf{r}) = \sum_i q_i + \sum_{i<j} q_{ij} = N$$

The total charge is divided out in such a way that an amount q_i arises from each orbital density d_i and q_{ij} from each overlap density d_{ij}. These quantities, first proposed by McWeeny, are usually referred to as orbital and overlap populations. The idea of population analysis has been extensively developed by Mulliken [11] but the populations assigned to the various regions of space are not unique, depending entirely on the choice of the basis orbitals; it is therefore clear that the nature of chemical bonds cannot be studied simply from an inspection of bond populations.

I.3.1.5 Valence Bond method.

The HF model is not apt to describe the splitting of a molecule into two parts when a bond is broken. The resulting pieces, in fact, are open-shell systems and are therefore badly described by single determinants of doubly occupied orbitals.

A better treatment of this phenomenon is given by the Valence Bond theory where each electron occupies an atomic orbital and each chemical bond is associated with the pairing of the spins of two-electrons in the valence orbitals of the atoms they belong to; for a polyatomic molecule with N singly occupied valence atomic orbitals, $\varphi_1, \varphi_2, ..., \varphi_N$, the orbital product function $\varphi_1(\mathbf{x}_1)\varphi_2(\mathbf{x}_2)...\varphi_N(\mathbf{x}_N)$, is combined with a singlet spin factor $\alpha\beta - \beta\alpha$ for any pair describing a bond and an α factor for any

single or parallel coupled electron. The Pauli principle is satisfied applying the usual antisymmetrizer $\hat{A} = \sum_P \epsilon_P P$ defined in Eq.I.3.1.4c.

With neglect of overlap one may define

$$Q = < \varphi_1\varphi_2...\varphi_N|\hat{H}|\varphi_1\varphi_2...\varphi_N >$$

and

$$K_{ij} = < \varphi_1\varphi_2...\varphi_i...\varphi_j...\varphi_N|\hat{H}|\varphi_1\varphi_2...\varphi_j...\varphi_i...\varphi_N >$$

and obtains the energy expectation value

$$E = Q + \sum_{(ij)paired} K_{ij} - \frac{1}{2} \sum_{(ij)uncoupled} K_{ij} - \sum_{(ij)parallel} K_{ij} \qquad \text{(I.3.1.9)}$$

This formula gives the "perfect pairing" approximation, using one electronic configuration corresponding to the spin coupling scheme associated with a hypothetical allocation of chemical bonds. When a single configuration does not give an adequate picture of the bonding, all the plausible structures are admitted with various pairing schemes and the wavefunction is represented as a linear combination. The optimal mixing coefficients are obtained, as usual, by solving a matrix secular equation. At large distance, after breaking a bond, a correct wavefunction is obtained, describing isolated pieces of the molecule.

The main difficulty of this method consists in taking into account orbital overlap, which greatly increases the mathematical complexity. This is why the method has been displaced with the development of ab initio methods of computation. Several forms of the theory are now available, able to face this problem and indicating promising developments.

I.3.1.6 Correlation.

Another limit of the HF theory arises in the treatment of electron correlation. Two electrons cannot occupy the same region in space (Coulomb Hole). This correlation is foreseen by the HF model only for electrons with parallel spin (Fermi Hole),

due to the antisymmetry of the wavefunction, but it is not considered for electrons with opposite spins and introduces an error of roughly one per cent; unfortunately, this corresponds to energy differences comparable, for example, with molecular binding energies, barrier heights, molecular interaction energies that the theory should be able to predict. The correlation energy is usually defined as the difference between the exact energy and the best one-determinant total energy.

The greatest efforts have been employed by theoretical chemists to study the correlation problem.

Three main methods have been applied:

(i) one can determine the coefficients of a CI expansion directly, along with the first few energy levels, by direct solution of the secular equation, using the most powerful tecniques available for evaluating matrix elements and solving the matrix eigenvalue problem;

(ii) long CI expansions can also be handled by starting from a leading term Φ_0, which would be an exact eigenfunction of a model hamiltonian H_0, and regarding $H - H_0$ as a perturbation under whose influence the remaining CI coefficients will assume non-zero values, which can be estimated by many-body perturbation theory [12], using diagrammatic tecniques, without actually solving secular equations. Rayleigh-Schrödinger perturbation theory [7], where the energy is expanded in terms of sum-over-states formulae, forms the basis of many-body perturbation theory; cancellation of unphysical, non-linear terms in the sum-over-the states formulae is a feature of many-body formalism within the algebraic approximation, i.e., by using finite analytic basis sets. The Møller-Plesset perturbation theory [13], is essentially one form of this perturbation approach and is now widely used. Taking a single-determinant Φ_0 as reference function for the CI expansion $\Psi = \Phi_0 + \sum_{\chi>0} C_\chi \Phi_\chi$, the remaining terms Φ_χ are taken to be single determinants with single, double and multiple "excitations" from the occupied orbitals of Φ_0 to a complementary set of virtual orbitals. This expansion is in principle exact. By making a particular choice of SO's in Φ_0,

single excitations can be eliminated; for electrons double excitations are of the greatest importance, higher-order corrections to the wavefunction being well expressed as antisymmetrized products of them. Such an approach leads to a Correlated Electron Pair Approximation, CEPA [14], of which there are many varietes; if higher-order corrections are neglected, i.e. the electron pairs are considered completely independent, an Independent Electron Pair Approximation, IEPA [15], results in which the correlation energy, at least formally, can always be expressed as a sum of electron pair contributions. A separate Schrödinger equation is then solved for each electron pair, and in first approximation the resulting pair correlation energies are simply summed to give an estimate of the total correlation energy.

(iii) A system can be formally divided into weakly interacting subsystems, correlation being calculated by CI within each subsystem (Group Function Approach). This method is conceptually different from the other illustrated in (i) and (ii) because it stresses the importance of local contributions to the properties of the whole molecule. The group wavefunctions, each one describing a group of electrons, are usually built up by making an a priori assumption of localization of the electrons. For example, we can suppose that two-electron groups are able to represent bonds. If every bond orbital is built as a linear combination of two one-electron wavefunctions, a bonding (r_1) and an anti-bonding (r_2) orbital, then the antisymmetric group function Φ_R can be defined as

$$\Phi_R = N_R(||r_1\bar{r}_1|| + \lambda^R||r_2\bar{r}_2||)$$

where N_R is a normalization factor. The total wavefunction is an antisymmetric product of group functions

$$\Psi = \hat{A}[\Phi_A\Phi_B...\Phi_R...]$$

where $\hat{A} = \sum_T \epsilon_T T$, T being a transposition which exchanges variables between different groups. The wavefunction Ψ can be expanded following from the definition of the group functions Φ_R:

$$\Phi_R = \frac{N_R}{\sqrt{2}}[r_1 r_1(\alpha\beta - \beta\alpha) + \lambda^R(r_2 r_2(\alpha\beta - \beta\alpha))]$$

$$\Psi = c^0\{\hat{A}'[a_1\bar{a}_1 b_1\bar{b}_1 ... r_1\bar{r}_1 ...] + \sum_R \hat{A}'[\frac{a_1\bar{a}_1 b_1\bar{b}_1 ... r_1\bar{r}_1 ...}{r_1\bar{r}_1} r_2\bar{r}_2]c_R +$$

$$\sum_R \sum_{S\neq R} \hat{A}'[\frac{a_1\bar{a}_1 b_1\bar{b}_1 ... r_1\bar{r}_1 ... s_1\bar{s}_1 ...}{r_1\bar{r}_1 s_1\bar{s}_1} r_2\bar{r}_2 s_2\bar{s}_2]c_{RS} + ...\}$$

In this case the antisymmetrizer is $\hat{A}' = \sum_P \epsilon_P P$ where P is any permutation between the variables and $c^0 = \Pi_R(\frac{N_R}{\sqrt{2}})$. The first term in Ψ is a Slater determinant Φ built up from the one electron functions $\{r_1\}$, the remaining terms are wavefunctions obtained from Φ on replacing $r_1\bar{r}_1$ by $r_2\bar{r}_2$, i.e., by double substitutions, or by quadruple substitutions and so on, and they give rise to the correlation energy.

I.3.1.7 Localized Orbitals.

Molecular calculations would stand to gain considerable intuitive appeal if they contained some direct recognition of localized bonds [4,2c,16].

Local bond functions were naturally employed in the valence-bond theory of molecular electronic structure [6]: each bond was described as a two-electron closed-shell system with an antisymmetric spin function, $\frac{1}{\sqrt{2}}(\alpha\beta - \beta\alpha)$ and a symmetric spatial function assumed as a linear combination of aa, bb and $\frac{1}{\sqrt{2}}(ab + ba)$, a and b being atomic wavefunctions for the two atoms of the bond respectively.

The definition of equivalent orbitals by Coulson, Hall and Lennard-Jones following from the fact that the solutions of the HF equations for a closed-shell system are determined except to a unitary tranformation among the occupied orbitals showed the possibility of an MO description of bonds at the HF level [17]. A unitary transformation can be chosen so that the resulting MO are localized (Localized Molecular Orbitals, LMO) and, where symmetry allows, equivalent. The equivalent orbitals

share the permutation properties of bonds, being inconverted by the symmetry operations of the molecular point group, and are highly localized in the bond regions. Lennard-Jones and Pople suggested that, since equivalent orbitals are highly localized, an electron occupying one of them would have maximum Coulomb interaction with the electron sharing that orbital . Edmiston and Ruedenberg used this idea and devised an iterative numerical method for implementing this self-energy localization criterion also for cases where symmetry equivalence could not be defined [18]. A steepest-ascents method has also been suggested [19]. Foster and Boys thought of localized orbitals which minimize the sum of separations between orbital centroids of charge [20]. This type of localization has been called an "intrinsic localization" criterion since it in no way it depends on the LCAO basis. Another intrinsic criterion is due to von Niessen. The von Niessen or Density criterion makes use of the electron density operator maximizing the self-overlaps of the LMO densities [21].

There have also been proposed other localization criteria schemes, particularly of the "extrinsic criterion" type: they depend on the nature of the LCAO basis set used. Cutting delocalization tails is the most expeditious process to prevent the electrons described by an LCAO wavefunction from diffusing outside some molecular domain [22]: thus, for example, Peters demanded that bond orbitals contain no contribution from basis function on atoms not participating in the bond. Overlap criteria for localization are of interest since their definition need not involve the troublesome two-electron integrals. Del Re et al. required that hybrids in a local bond orbital have minimum overlap with the hybrids associated with other bonds [23]. Magnasco and Perico defined as a measure of the localization the population of orbitals in local sets of basic functions, appropriate to individual bonds [24]. Recently Rajzmann and Purcell [25] minimize the sum of the "remote population", calculated in the same way as the population, but over unoccupied MO's and Pipek and Mezey [26] have proposed an intrinsic method called "population localization" which minimizes a measure of the mean extension of the MO's (delocalization) calculated from the gross Mulliken population. Other localization criteria utilize the properties of the

density matrix [27]. Projection methods give a set of quasi localized orbitals. The principle is as follows: a set of ad hoc completely localized orbitals is projected into the space spanned by the primitive delocalized orbitals, and the resulting orbitals are reorthogonalized by the Löwdin transformation, giving the final set of quasi-localized orbitals [28].

The direct calculation of local orbitals has been discussed by Edminston and Ruedenberg [18] and in more details by Gilbert [29], Adams [30], Peters [31], Wilhitte and Whitten [32], Daudey [33], Letcher and Dunning [34], Anderson [35], von Niessen [36], Huzinaga [37]. There are also the so called 'bond functions' which are not centered on any of the atoms, but are placed between two neighbouring ones to represent bonds [38]. These direct localization schemes, though they are certainly very important from the theoretical point of view, did not help too much in practical applications.

The concept of localized orbitals goes far beyond the framework of the pure HF theory: it can also be used in connection with correlated functions [39,33].

Strictly Localized Molecular Orbitals (SLMOs) can be determined a priori without referring to the exact Hartree-Fock orbitals [2] by assigning basis functions to bonds. Each SLMO in a bond (Strictly Localized Geminal, SLG) can be expanded within the subspace of basis orbitals assigned to the bond in question. The best (optimized) SLGs are obtained by determining the expansion coefficients variationally, yielding an energy minimum for the many-electron determinantal wavefunction built up by the set of SLG. The corresponding formalism is in close relationship with the Group Function method. In fact the present theory is a special case of theformer where fragments are not necessarily identified with two-centre subunits. We will describe Group Function Theory in the next Chapters. This a priori inductive treatment will be discussed in section I.4, but an important tool to derive such orbital sets must be introduced now, that is hybridization [2d,40-43]; this involves a unitary transformation of the basis orbitals which mixes only orbitals assigned to the same atom. Usually it does not affect the inner shell orbitals, while the valence shell AO's are

transformed into orbitals which are directed towards two-centre bonds or lone pairs.

Pauling formulated the first definitions of hybrid orbitals (HAOs) [6]. His analysis of the bond revealed that the bond is stronger if the concentration of orbitals in the internuclear region is greater and he was the first who discussed the principle of maximum overlapping. However, instead of calculating overlap integrals, he defined the bond strengths of the orbital as the maximum value of the angular part of the orbital function normalized to 4π over the surface of a sphere.

Since the l-quantization does not hold anymore in perturbed atoms embedded in the intramolecular field, one can freely mix s, p, d, f... AO's. Assuming hybrid orthonormality and employing a maximum bond strength criterion, equivalent tetrahedral sp^3 hybrids are easily constructed:

$$\chi_1 = \tfrac{1}{2}[(ns) + (np_x) + (np_y) + (np_z)]$$

$$\chi_2 = \tfrac{1}{2}[(ns) + (np_x) - (np_y) - (np_z)]$$

$$\chi_3 = \tfrac{1}{2}[(ns) - (np_x) + (np_y) - (np_z)]$$

$$\chi_4 = \tfrac{1}{2}[(ns) - (np_x) - (np_y) + (np_z)]$$

Pauling observed that the degree of hybridization, when it is not determined purely by symmetry, for example in the presence of lone pairs, is strongly dependent on the (ns)-(np) energy gap, being most effective for the first row atoms where the gaps are small.

For an hybrid orbital the s-character can be defined as

$$(s\%) = \frac{c^2(2s)}{c^2(2s) + c^2(2p_x) + c^2(2p_y) + c^2(2p_z)}$$

where the $c(2s)$, $c(2p_x)$, $c(2p_y)$, $c(2p_z)$ are the coefficients multiplying respectively the $2s$, $2p_x$, $2p_y$, $2p_z$ AO in the hybrid definition. This index can be used for studying the similarity among different hybrids and it is a measure of the bond strength of the hybrid orbital. The bond strength increases as the s-character decreases.

Interestingly, Pauling explained double and triple bonds by two tetrahedra sharing a common edge and side, respectively [40], i.e., by two bent bonds, where the electron density is concentrated in two regions of space more distant from each other than in a $\sigma - \pi$ description. The structure with bent bonds can be, therefore, the energetically favoured.

Duffey and co-workers used the criterion of maximum amplitude in studying a number of large molecules [44].

Apart from the maximum amplitude criterion, there are many other ways of constructing local hybrids AO's. One of them is the Localized Atomic Orbital (LOA) method designed by Aufderheide and Chung-Phillips [45]. They maximize the function L_A for each atom A, where

$$L_A = \sum_{\mu}^{A} \sum_{\lambda}^{occ} \sum_{\sigma}^{occ} \frac{1}{4} P_{\mu\sigma} P_{\lambda\mu} < \chi_\mu(1)\chi_\lambda(2)|r_{12}^{-1}|\chi_\mu(1)\chi_\sigma(2) >$$

and $P_{\mu\sigma}$ denotes the conventional bond order matrix. The basis set orbitals $\{\chi_\mu\}$ which yield maximal value of L_A are local orthogonal hybrid orbitals. In a calculation on H_2O two 'rabbit-ear' lone pairs result; and the lone pairs hybrids are found to have a higher s-content.

In the Generalized Valence Bond (GVB) method, hybridization follows as a consequence of the full variational calculation and is not introduced as an a priori postulate. Essentially the GVB wavefunction can be viewed as generalization of a closed-shell HF function $\hat{A}(\psi_1\bar{\psi}_1\psi_2\bar{\psi}_2...)$ where $\hat{A}$ represents a customary antisymmetrizer, in which each pair of orbitals is replaced by $\psi_i\bar{\psi}_i \quad \rightarrow \quad (\psi_{ia}\psi_{ib} + \psi_{ib}\psi_{ia})\alpha\beta$ where the first position in products implies electron 1 and the second electron 2.

A large number of molecules have been treated by the GVB procedure and the corresponding hybrids are available [46]. Using this method Messmer et al. have shown that a bent bond picture describes multiple bonds in CO_2, C_2H_4, and C_2H_2 better than the more common σ- and π-orbitals, in line with Pauling's early conjec-

tures. Inclusion of correlation between pairs of coupled electrons makes the bent bond picture even more accurate [47]. We shall use a similar model within the Group Function formalism in the second part of the present work. The localized orbital picture retains its validity even in archetypal delocalized molecules like benzene, pyridine and the related six-membered rings [48]. It appears that aromatic stability arises more from the mode of spin coupling than from orbital delocalization.

Another way of extracting hybridization parameters from molecular wavefunctions is by making use of the first order density matrix. Let us first consider the early prescription of McWeeny and Del Re [49].

Starting with AO's after Löwdin orthogonalization, the localized bond formed by coupled hybrids orbitals χ_r and χ_s takes the form $\cos\theta_{rs}\chi_r + \sin\theta_{rs}\chi_s$, where θ_{rs} is the ionic-character parameter. McWeeny-Del Re method implies a unitary transformation of inital pure AO's and subsequent SCF calculations. A matrix $\tilde{\mathbf{P}}$ can be defined

$$\tilde{\mathbf{P}} = \begin{array}{c} \\ r \\ \\ s \\ \\ t \end{array} \begin{array}{c} \begin{array}{ccccccc} & & r & & s & & t \end{array} \\ \begin{pmatrix} \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \cdots & 1+\cos 2\theta_{rs} & \cdots & \sin 2\theta_{rs} & \cdots & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \cdots & \sin 2\theta_{rs} & \cdots & 1-\cos 2\theta_{rs} & \cdots & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \cdots & \cdots & \cdots & \cdots & \cdots & 2 \end{pmatrix} \end{array}$$

where $\tilde{P}_{tt} = 2$ describes the lone pair corresponding to two coinciding hybrids. If $\theta_{rs} = 45^o$ one has a purely covalent bond where $P_{rr} = P_{ss} = P_{rs} = P_{sr} = 1$. In general, neither the hybrids are completely localized nor the bonds are 100% covalent. However HAO's can be constrained to satisfy one or both of these conditions leading to an increase in total energy of a molecule. In this way effects of ionicity and delocalization can be extimated.

Foster and Weinhold diagonalize atomic blocks of the $\tilde{\mathbf{P}}$ matrix, obtaining natural

hybrid orbitals [50]. Similarly, if one diagonalize extended submatrix associated with bonded atoms, one obtains eigenfunctions describing bond orbitals.

Instead of diagonalizing the density matrix $\tilde{\mathbf{P}}$, a straightforward calculation of hybrid s- and p-character is possible [51]. The idea was based on an early observation of Wiberg that the square of the bond order in CH bonds is related to their s-character. The bond charge can be expressed as:

$$W^{AB} = 2\sum_{\nu}^{A}\sum_{\mu<\nu}^{B} P_{\mu\nu}S_{\mu\nu}.$$

The bonding charge of all four 2s and 2p AO's of the atom A taking part in the $A-B$ bond is $\frac{1}{2}W^{AB}$. Defining $W_{s(AB)}$ as the part of the $2s_A$ orbital involved in the $A-B$ covalent bond $W_{s(AB)} = \sum_{\nu}^{B} P_{2s_A\nu}S_{2s_A\nu}$, the s-character of the χ_{AB} hybrid is given by:

$$W_s^{AB} = \frac{W_{s(AB)}}{(1/2)W^{AB}}$$

The first general method for constructing hybrid orbitals used the maximum overlap condition. Maximum overlap molecular orbitals (MOMO) received a detailed description and this method is easily implemented even in largest systems.

Del Re discussed a way of obtaining hybrid orbitals AO's within the framework of the effective one-electron hamiltonian where the wavefunctions are expressed in a form of linear combination of atomic orbitals, solving by a unitary transformation of the pure AO's so that the overlap matrix has the pseudo-diagonal 2×2 form as close as possible [52], the equation

$$\tilde{\mathbf{H}}\tilde{\mathbf{C}} = \tilde{\mathbf{S}}\tilde{\mathbf{C}}\tilde{\mathbf{E}}$$

where $S_{ij} =< \theta_i|\chi_j >$, θ_i being a ligand orbital in a system of the type $M(x_1, ...x_k)$ and χ_j being an orbital om atom M.

In the Iterative Maximum Overlap (IMO) Method [53] a basis set of local hybrid

orbitals

$$\chi_i = a_i(2s) + (1 - a_i)^{1/2}(2p)_i$$

is varied until the sum of bond energies E_b is maximized.

A plausible assumption that the bond energies are linear functions of the corresponding overlap integrals $E_{AB} = k_{AB}S_{AB} + l_{AB}$ is made, where k_{AB} and l_{AB} are empirically adjusted parameters. The hybridization indices a_i are subject to orthonormality conditions

$$a_i a_j + (1 - a_i^2)^{1/2}(1 - a_j^2)^{1/2} \cos\theta_{ij} = \delta_{ij}$$

for $i, j = 1...4$, where θ_{ij} is the angle between the axial symmetric hybrids ψ_i and ψ_j sharing the same atom. During the calculations the HAO's are allowed to follow the directions of the straight lines passing through the directly bonded nuclei. To be quite precise, bond angles are determined by the interhybrid angles θ_{ij} of the optimal hybrids. Orthogonality and perfect orbital following of hybrids are not completely justified suppositions but they work very well in most cases. They considerably add to the simplicity of the method.

Finally, interatomic overlap integrals are forced to follow a predetermined linear bond overlap/bond distance correlations.

In the first iterative step the initial bond distances are selected by an educated guess and the independent hybridization parameters a_i are varied until the maximum of E_b is achieved. Then the next set of bond distances is deduced and the hybridization indices are reoptimized. The whole iterative procedure is repeated until a consistency between the input and the output bond distances is extablished. Hence, the IMO scheme is a constrained weighted maximum overlap method.

I.3.2 Semiempirical Developments.

Ab initio calculations, especially at a correlated level, are very expensive in terms of computer memory requirements and are time consuming, when the number of elec-

trons increases. In fact the number of integrals necessary to perform a single calculation depends on the fourth power of the number of orbitals; moreover, the number of iterations needed to reach convergence can be very high. For such reasons, many semiempirical methods have been introduced, in which some quantum mechanical quantities are replaced by empirical quantities.

Semiempirical calculations employing the MO method have been widely applied to organic molecules [54]. For a long time they were applied to only the π electrons of conjugated molecules using a simple theoretical model due to Hückel [55] where the matrix elements are defined as

$H_{\mu\mu} = \alpha$

$H_{\mu\nu} = \beta$ if μ and ν belong to bond atoms,

$H_{\mu\nu} = 0$ otherwise

where α and β, the coulomb and resonance integral respectively, are determined empirically by fitting the results to observed data and $S_{\mu\nu} = \delta_{\mu\nu}$. The first consistent improvement of the Hückel method due to Pople and Parr and Pariser (the so-called PPP method) [56-57] utilized the LCAO approximation within the HF method applied to the π system and introduced electron interaction. Later, in a historically very important paper, Sandorfy applied Hückel theory to saturated hydrocarbons, for the first time including the hydrogens, and concluded that MO methods of the LCAO type would be capable of giving a good charge distribution in such molecules as many did for conjugated systems [58]. The LCAO may be that of the regular atomic orbitals, such as the 2s and 2p and the hydrogen 1s, or of hybridized valence orbitals (LCVO). Fukui and coworkers in their pioneering applications used especially an LCVO method without overlap [59]. A hybrid-based MO theory, but including electron-electron repulsions has been given by Katagiri and Sandorfy [60]. A strong impetus to the treatment of large systems has developed from the extended Hückel theory work of Hoffmann [61], where all the one-electron matrix elements $H_{\mu\nu}$ and all the overlaps $S_{\mu\nu}$ were included. Another much simplified method, the subminimal ab initio method

of Frost also gives remarkable success in the prediction of geometries. The full exact hamiltonian and all the matrix elements that it gives rise to are used, but, in turn, the orbitals themselves are chosen in the simplest possible manner [62]. The Hückel type methods do not include electron-electron interactions and the adjustments of the parameters that would result from them. One way to go beyond the Hückel method while retaining its basic simplicity and lack of difficult integrals has been to introduce iterations to the parameters, dependent on charge distribution (Iterated Extended Hückel Calculation (IEHC)) [63]. A very importrant development in $\sigma - MO$ theory involved the inclusion of electron-electron repulsions to achieve a self-consistency of the orbitals. A number of versions of approximate SCF methods have been developed.

In all of them the elimination of direct reference to inner shell electrons forms the basis of the so-called all-valence-electrons approximation: the molecular electrons should comprise subset A, the inner shell electrons of all atoms in the molecule, described by Ψ_A, and subset B, the atomic valence shell electrons, described by Ψ_B, where we assume that these subsets are separable. Experiments indicate that inner shell electrons are relatively inert in typical chemical processes. Thus, we expect that the assumption of a fixed Ψ_A should not lead to significant errors. Moreover, Ψ_A should not depend on the state of the valence shell electrons. Thus the inner shell electrons represent only the source of electrostatic potential for valence shell electrons and simply screen the field of nuclear charges. In a very crude approximation, the inner shell electrons may be effectively eliminated by substituting the atomic core charges Z'_k for the corresponding nuclear charge in the hamiltonian operator. The core hamiltonian obtained in this way represent the total energy operator for an electron moving in the field of N atomic cores with charges Z'_k:

$$\hat{h}^c(1) = -\frac{1}{2}\nabla^2(1) - \sum_{k=1}^{n_C} \frac{Z'_k}{r_{1k}} =$$

$$= -\frac{1}{2}\nabla^2(1) - \sum_{k=1}^{n_C} V_k(1)$$

where n_C is the number of core orbitals.

In general the core hamiltonian is an effective hamiltonian

$$\hat{h}^c(1) = -\frac{1}{2}\nabla^2(1) - \sum_{k=1}^{n_{at}} \frac{Z_k}{r_{1k}} + \sum_{k_C=1}^{n_C} (J^C(1) - K^C(1))$$

where the coulomb and exchange core operators $J^C(1)$ and $K^C(1)$ describe the effective field generated by the core orbitals to which valence electrons are subjected. In this way inner shell electrons may be eliminated from the calculation if valence orbitals are orthogonal to core orbitals.

Approximate semi-empirical HF schemes employing the all-valence-electron approximation can be classified, according to Pople et al. [64] depending on the use they make of the Zero Differential Overlap (ZDO) approximation, which assumes that

$\phi^*_{\mu A}(1)\phi_{\nu B}(1) = 0$ for $\mu_A \neq \nu_B$

where $\phi_{\mu A}$ is the μ-th orbital of atom A and $\phi_{\nu B}$ is the ν-th orbital of atom B.

(i) In the NDDO (Neglect of Diatomic Differential Overlap) Method the ZDO approximation is used for all overlap integral. The three- and four-centre integrals are neglected. For two-electron integrals, ZDO is assumed valid when the atomic orbitals ascribed to a given electron belong to different atoms.

(ii) In the INDO (Intermediate Neglect of Differential Overlap) Method as in (i) the ZDO approximation is used for all overlap integral and the three- and four-centre integrals are neglected. Among the two-electron, two-centre integrals those of non-coulombic type are eliminated, although all one-centre two-electron are retained.

(iii) In the CNDO (Complete Neglect of Differential Overlap) Method the ZDO approximation is employed for all two-centre orbital products in both overlap and two-electron integrals.

The introduction of the ZDO approximation has lead to the complete neglect of overlap integrals, and thus these methods treat the atomic orbitals as orthogonal.

The overlap integral may equal zero even if the integrand does not vanish over the whole space. Sometimes calculations are performed by imposing the weaker condition that only the corresponding overlap integrals vanish. To distinguish this method from the ZDO approximation we say that the zero overlap approximation is used.

The particular variants of semi-empirical NDDO, INDO and CNDO schemes differ in the way some non-empirical quantities are replaced by appropriate parameters.

The HF operator is invariant with respect to an arbitrary unitary molecular orbital transformation. In semi-empirical methods a slightly different invariancy condition has been proposed: the same results, using the same approximations, should be obtained for different AO bases related to one another either by a unitary or orthogonal transformation. This type of invariance requirement is only formal; it makes the approximations independent of the basis used, but it is not a true physical invariance condition. Disregard, in semi-empirical methods, of the invariance condition with respect to unitary transformation of the basis set may lead to unphysical results (i.e. dependence of the electron density distribution, dipole moment or total energy on choice of coordinate system). Other approximations could have to be added in order to satisfy the invariance condition.

(i) The NDDO approximation does not violate the assumed invariance principle since each atom has its whole valence shell taken into account.

$$F_{\mu_A\nu_A} = H^C_{\mu_A\nu_A} + \sum_{\lambda_A,\sigma_A} P_{\sigma_A\lambda_A}[(\mu_A\nu_A|\lambda_A\sigma_A) - \frac{1}{2}(\mu_A\sigma_A|\lambda_A\nu_A)] +$$

$$+ \sum_{C\neq A}\sum_{\lambda_C,\sigma_C} P_{\sigma_C\lambda_C}(\mu_A\nu_A|\lambda_C\sigma_C)\delta_{\mu_A\nu_A}$$

$$F_{\mu_A\nu_B} = H^C_{\mu_A\nu_B} - \tfrac{1}{2}\sum_{\lambda_B\sigma_A}(\mu_A\sigma_A|\lambda_B\nu_B) \text{ for } B \neq A$$

The matrix elements of the core operator are

$$H^C_{\mu_A\nu_A} = U_{\mu_A\nu_A} - \sum_{C\neq A} < \mu_A|V_C|\nu_A >$$

where $U_{\mu_A\nu_A} =< \mu_A| - \frac{1}{2}\nabla^2 - V_A|\nu_A >$.

Thus, in the NDDO scheme, all integrals which contribute to the element $H^C_{\mu_A\nu_A}$ must be considered, since these are at most two-centre ones,

$H^C_{\mu_A\nu_B} =< \mu_A| - \frac{1}{2}\nabla^2 - V_A - V_B|\nu_B >$ for $B \neq A$.

(ii) in the INDO method the following approximations are added to fulfill the invariance condition:

1. All two-centre Coulomb integrals are made independent of the type of atomic orbitals,

$(\mu_A\mu_A|\nu_B\nu_B) = \gamma_{AB}$ for $B \neq A$

The two-centre integral γ_{AB} will thus depend solely on the nature of the atoms A and B.

2. $< \mu_A| - \frac{1}{2}\nabla^2 - V_A|\nu_A >= U_{\mu_A\mu_A}\delta_{\mu_A\nu_A}$

for non-hybridized orbitals, since for $\mu_A \neq \nu_A$ the product $\phi_{\mu_A}\phi_{\nu_A}$ is not fully symmetric, and

$< \mu_A|V_B|\nu_A >=< \mu_A|V_B|\mu_A > \delta_{\mu_A\nu_A}$

3. The remaining integrals $< \mu_A|V_B|\mu_A >$ do not depend on the type of atomic orbital μ_A, i.e.,

$< \mu_A|V_B|\mu_A >= V_{AB}$

4. $H^C_{\mu_A\nu_B} =< \mu_A| - \frac{1}{2}\nabla^2 - V_A - V_B|\nu_B >= \beta_{\mu_A\nu_B}$ resonance integral, empirical parameter.

Taking into account all the INDO assumptions, we obtain the matrix elements of the HF operator,

$$F_{\mu_A\nu_A} = U_{\mu_A\mu_A}\delta_{\mu_A\nu_A} + \sum_{\lambda_A,\sigma_A} P_{\sigma_A\lambda_A}[(\mu_A\nu_A|\lambda_A\sigma_A) - \frac{1}{2}(\mu_A\sigma_A|\lambda_A\nu_A)] +$$

$$+[\sum_{B\neq A}(P_{BB}\gamma_{AB} - V_{AB})]\delta_{\mu_A\nu_A}$$

where $P_{BB} = \sum_{\lambda_B} P_{\lambda_B\lambda_B}$

$F_{\mu_A\nu_B} = \beta_{\mu_A\nu_B} - \frac{1}{2}P_{\mu_A\nu_B}\gamma AB$ for $B \neq A$

(iii) One- and two-centre two-electron integrals which do not vanish by virtue of the ZDO approximation are independent of atomic orbital type, i.e.

$(\mu_A\mu_A|\lambda_A\lambda_A) = \gamma_{AA}$

$(\mu_A\mu_A|\mu_B\mu_B) = \gamma_{AB}$

The approximation concerned with matrix elements of the core Hamiltonian are identical to those of the INDO scheme.

$$F_{\mu_A\nu_A} = U_{\mu_A\nu_A} + P_{AA}\gamma_{AA}\delta_{\mu_A\nu_A}\frac{1}{2}P_{\mu_A\nu_A}\gamma AA +$$

$$+[\sum_{B\neq A}(P_{BB}\gamma_{AB} - V_{AB})]\delta_{\mu_A\nu_A}$$

$F_{\mu_A\nu_B} = \beta_{\mu_A\nu_B} - \frac{1}{2}P_{\mu_A\nu_B}\gamma AB$ for $B \neq A$

Experimental data on isolated atoms will provide a direct source of at least some one-centre quantities, i.e. the integrals $U_{\mu_A\mu_A}$ and $(\mu_A\sigma_A|\lambda_A\nu_A)$, called therefore atomic parameters. Two-centre integrals such as $(\mu_A\mu_A|\nu_B\nu_B)$,V_{AB} or $\beta_{\mu_A\nu_B}$ (referred to as molecular parameters) play the role of direct empirical parameters to a much smaller degree. Two-centre two-electron integrals are often calculated from

their definitions and the assumed AO basis. In parametrization, one should try to employ numerical experimentation or to refer to simple physical model and intuition.

Each specific semi-empirical realization of the approximate HF method can be completely characterized by different definitions of the following elememts:

A. The form of the assumed AO basis.

B. The parameters $U_{\mu_A \mu_A}$.

C. The one-centre two-electron integrals.

D. The calculation or approximation of two-electron Coulomb integrals γ_{AB}.

E. The calculation or approximation of resonance integrals $\beta_{\mu_A \nu_B}$.

F. The approximation of the core-core repulsion energy

A great number of different parametrizations have been studied, particularly for the CNDO and INDO schemes [54,65].

I.4 The Relevant Fragment and its Environment

In many cases it is advantageous to partition the extended system into different regions. One needs the highest accuracy in the description of the subsystem of interest, and lesser precision might be sufficient for parts of the system which play a secondary role [2e].

The building blocks for describing the system should be chosen to be so weakly interacting that various physical properties are nearly additive in term of the block contributions. This does not imply that such contributions are strictly transferable. In fact, the extent of transferability is usually smaller than that of additivity.

Individual molecules, when not too large, are very suitable building blocks; but for very large molecules one should find some intramolecular constituents which could play the role of building units, like functional groups. The concept of localized bonds remains an essential ingredient of the theory and it will also prove to be useful for the definition of larger fragments [66,2f] because global molecular properties (energy, dipole moments,...) can be well described in terms of bond contributions.

We are mainly interested in an a priori inductive treatment of chemical bonding, that is a constructive approach in which the wavefunctions of individual chemical bonds are calculated and general tendencies are inferred on the basis of these calculations. This approach also has the advantage that approximate many-electron wavefunctions can be constructed in terms of local two-electron functions. The discussion of localized bonds can be easily generalized to study larger fragments (functional groups, etc.) in molecules.

Some of the most important fragment theories are [2f]:

a) McWeeny's group function formalism [see later on],

b) Diatomics-in-molecule (DIM) methods [2g],

c) the PCILO idea [67],

d) perturbation theories for constructing LMO's [68] and d') the related geminal-type models [69],

e) Mehler's non-orthogonal group function method [70],

f) Kirtman's density matrix treatment [71],

g) the Fragment SCF methods (FSCF) [72,93,106],

h) various other group function techniques [73].

These methods are briefly examined in the following pages.

a) McWeeny's group function formalism is developed in detail in the second part of this thesis.

b) Diatomics in molecule (DIM) method states that the Hamiltonian matrix elements of the polyatomic molecule are expressed in terms of the matrix elements of diatomic and atomic hamiltonians in a corresponding basis. This is possible because both the polyatomic and diatomic bases are constructed from a set of functions X(M), where M=1,...,N_x and N_x is the number of polyatomic basis functions, which are antisymmetric products of atomic functions. The hamiltonian matrix in the function can be expressed in terms of diatomic and atomic fragment matrices in the related basis by utilizing the (exact) partitioning of the polyatomic hamiltonian operator

$$\hat{H} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \hat{H}_{ij} - (N-2) \sum_{i=1}^{N} \hat{H}_i$$

where N is the number of atomic centres.

The MM' matrix element $< X(M')|\hat{H}|X(M) >$ is expressed as a sum of fragment terms by applying the partitioning of the polyatomic hamiltonian appropriate to the electron distribution implied by the index M.

Along the same lines, a Molecule in Molecule (MIM) method can be developed [74].

c) The PCILO idea [67] employs localized molecular orbitals, linear combinations of a few atomic orbitals, describing chemical bonds and lone pairs, and a perturbation expansion at the configuration interaction level, subjected to the CNDO approximation.

The CI process is described by a wavefunction of the form

$$\psi_0 = c_0\phi_0 + \sum_I C_I\phi_I$$

where ϕ_0 is a self-consistent determinant, eigenfunction of an approximate hamiltonian, H_0, and ϕ_I are various excited determinants. If ϕ_0 is a good approximation to ψ_0, the exact ground state wavefunction, one may consider it as a zeroth-order wavefunction and get help from perturbation theory. To the zeroth-order energy the following corrections are added:

$$E_0^1 =< \phi_0|H - H_0|\phi_0 >$$

$$E_0^2 = \sum_I \frac{< \phi_0|H - H_0|\phi_I >^2}{E_0^0 - E_I^0}$$

$$E_0^3 = \sum_I \sum_J \frac{< \phi_0|H - H_0|\phi_I >< \phi_I|H - H_0|\phi_J >< \phi_J|H - H_0|\phi_0 >}{(E_0^0 - E_I^0)(E_0^0 - E_J^0)} +$$

$$+E_0^1 \sum_I (\frac{< \phi_0|V|\phi_I >}{E_0^0 - E_I^0})^2$$

The expressions of the perturbation corrections are greatly simplified if all ϕ_I are supposed to be eigenvectors of H_0. H_0 is usually chosen so that $E_0^1 = 0$ and the eigenvalues of H_0 for the ϕ_I are the corresponding mean values of the exact hamiltonian

$$H_0\phi_I = < \phi_I|H|\phi_I > \phi_I$$

For a localized set of MO's, the various excited determinants represent "local events". PCILO method is usually applied using CNDO approximations, which enormously simplify the form of the hamiltonian. In the special case where each bond is regarded as a neutral system (for a neutral molecule), each pair of electrons being balanced by two atomic nuclear protons, the total energy may be written as a sum

$$< \phi_0|H|\phi_0 >= \sum_i \epsilon_i + \sum_{i<j} \epsilon_{ij}$$

of one-bond energies involving a kinetic part plus the electrostatic interactions between the electrons and bond nuclear charges of each bond, and of two-bond energies, representing the electrostatic interactions between the charge distributions of the pairs of bonds. The energy has an additive local structure, and if the bonds i and j are transferable from one configuration of the molecule to the other or from one molecule to another, the terms ϵ_i, ϵ_j and ϵ_{ij} need not be recalculated. Only the interactions between bonds that are not in the same relative position have to be recalculated. This allows one to directly calculate the energy difference from one conformation to another.

d) perturbation theories for constructing LMO's [68] propose a special perturbation formalism for calculations of LMO's starting from a priori defined SLMO's and adding appropriate tails. Let us consider the bonding SLMO built up from two orthonormal atomic hybrids $|i_1 >$ and $|i_2 >$

$$\psi_i^0 = \frac{1}{\sqrt{1-q_i^2}}(|i_1> + q_i|i_2>)$$

Similarly, the antibonding orbital has the form

$$\psi_i^{0*} = \frac{1}{\sqrt{1+q_i^2}}(q_i|i_1> - |i_2>)$$

if i corresponds to a lone pair, $q_i = 0$ and ψ_i^{0*} is absent. The zeroth-order hamiltonian $\mathbf{H}^0$ consists of the intrabond matrix elements and it is diagonal assuming that the coefficients q_i in the first equation were determined variationally. Any other matrix element in $\mathbf{H}$ represents the perturbation

$$\mathbf{H} = \mathbf{H}^0 + \lambda \mathbf{H}^1$$

λ being the formal expansion parameter.

The expansion of the LMO's can be written as

$$\psi_i = \psi_i^0 + \sum_{\mu=1} \lambda^\mu \sum_k^{virt} c_{ik}^\mu \psi_k^{0*}$$

where the c_{ik}^μ are the expansion coefficients (tails) of order μ what we are looking for.

Similarly, the expansion of the antibonding orbital reads

$$\psi_i^* = \psi_i^{0*} - \sum_{\mu=1} \lambda^\mu \sum_l^{occ} c_{li}^\mu \psi_l^{0*}$$

The form of the virtual MO's keeps the occupied subspace orthogonal to the virtual one at any order of perturbation.

Then the expansion parameters can be determined from the block-diagonality requirement ("local Brillouin theorem") $< \psi_i|\hat{H}|\psi_j^* >= 0$ for every i, j pair of bonds.

The system can be solved at every order without considering any mixing between the bonding SLMO's. This is in accordance with the general theorem that there always exists a set of non-orthogonal localized MO's spanning the exact occupied space and having the property that each of them contains one and only one bonding SLMO.

d') perturbation theories for constructing geminal-type functions build a zeroth-order wavefunction Ψ^0 as an antisymmetrized product of two electron group wavefunctions (geminals) expanded in disjoint but overlapping subspaces of basis orbitals. A generalization of the non-degenerate Rayleigh-Schrödinger perturbation theory to the case of non-hermitian zeroth-order hamiltonian is considered, applying the method of moments [75] and putting $H = H^0 + W$. Since the total hamiltonian is hermitian but H^0 is not, W is not hermitian either. The zeroth-order wavefunctions Ψ^0 do not represent eingenfunctions from the left, neither form an orthogonal set. Using another set $\{\Phi^0\}$ of functions biorthogonal to the original ones $< \Phi^0_K | \Psi^0_L >= \delta_{KL}$, multiplying with those biorthogonal functions from the left and integrating, one obtains a straightforward generalization of the usual perturbation formulas.

e) Mehler's non-orthogonal group function (NOGF) method analizes intermolecular interactions relaxing the interorbital orthogonality. This allows the orbitals of different groups to be expanded within different subsets of the basis function spanning the total orbital space: the response of a given group to perturbations due to the presence of other groups is then limited by its subset of expansion functions. This additional degree of freedom in constructing the orbital, can then be used to decompose the interactions between the subsystems. In particular one can expand the orbital of a given group including basis functions from other groups. Then perturbation theory is applied directly to the NOGF pseudoeigenvalue equations.

f) Kitsman's density matrix treatment is a general method for determining the electronic structure changes when an extended system is disturbed by by a localized interaction. It is based on the density matrix formulation of the electronic structure problem.

The single particle density matrix $\mathbf{R}$ can always be written in the form $\mathbf{R} = \mathbf{R}_0 + \Delta\mathbf{R}$ where $\mathbf{R}_0$ represents the unperturbed matrix and $\Delta\mathbf{R}$ the correction due to the local interactions.

$$\Delta\mathbf{R} = \mathbf{R}_0\mathbf{X}_Q\mathbf{U}_0 + \mathbf{U}_0\mathbf{X}_Q\mathbf{R}_0, \qquad \mathbf{U}_0 = \mathbf{1} - \mathbf{R}_0.$$

$\mathbf{X}_Q$ is local by definition but it is, otherwise, arbitrary. In order to optimize this matrix we carry out a first-order perturbation treatment of the well known HF (or any other independent-particle model) stationary condition on $\mathbf{R}$.

This yields a linear matrix equation for $\mathbf{X}_Q$ in terms of the hamiltonian, which is tractable because the matrices are of the same dimensions of the local basis.

g) The Fragment SCF method (FSCF) proposes a model for the partitioning of very large molecular systems which has the advantage that the different regions can be treated at a gradually decreasing level of sophistication allowing one to reduce the computational work drastically. The system is divided into four regions. In the central region (C) the actual chemical changes (geometry distortion, bond fission, etc.) take place, and this is embedded successively in a delocalization (D), induction (I) and transferable (T) region respectively. The most important effect concerning region D is delocalization from and to C. In region I delocalization is neglected and only inductive effects are considered. Finally, region T is composed of fully transferable SLMOs and serves as a rigid, non-polarizable environment for regions C,D and I. The most convenient manner to describe these regions is to use SLMOs. The SLMOs can be expressed as linear combination of normalized atomic hybrids orbitals. Once we have the proper hybrid orbitals a zeroth-order wavefunction can be constructed from all occupied two-centre SLMOs. Once we have optimized parameters of the SLMOs, the MOs for region C can be expanded on this basis set.

The SLMOs can be expressed as linear combination of normalized atomic hybrid orbitals

$\phi_i^{\sigma} = C_{Ai}h_{Ai} + C_{Bi}h_{Bi}$ for a σ orbital,

$\phi_i^{lp} = h_{Ai}$ for a lone pair,

$\phi_i^{\pi} = \sum_{A=1}^{M_{\pi i}} C_{Ai}u_{Ai}^{n_{p_z}}$ for a π orbital.

where h_{Ai} stands for a normalized hybrid orbital centered on atom A

$h_{Ai} = b_i^{n_s}u_A^{n_s} + b_i^{n_{p_x}}u_A^{n_{p_x}} + b_i^{n_{p_y}}u_A^{n_{p_y}} + b_i^{n_{p_z}}u_A^{n_{p_z}}$

where $u_A^{n_{p_x}}$,... are normalized Slater orbitals (when $A = H$, hydrogen, $h_{Ai} = u_A^{1_s}$).

$M_{\pi i}$ denotes the number of π centres in the i-th π-type molecular orbital.

We start with a set of hybrids with standard s-character and directed along the bonds. Such hybrids are not orthogonal on each atomic center (except in the case of some special bond angles), but a consecutive Löwdin-orthogonalization allows one to readjust their s-character and bond-directions. Once we have the proper hybrid orbitals a zeroth-order wavefunction can be constructed from all occupied two-centre SLMOs. To optimize their coefficients (which determine the bond polarities) the following coupled set of 2 × 2 secular equations can be devised [72].

$$F_i C_{mi} = \epsilon C_{mi}$$

where in practice the Fockian may be defined within the framework of the CNDO/2 approximation.

$$F_{aa,i} = H_{aa,i}^{eff} + \sum_{m=1}^{M} P_{mm,i}(ai;ai|mi;mi) - \tfrac{1}{2}(P_{mm,i} - 1)(ai;ai|ai;ai)$$

$$F_{ab,i} = H_{ab,i}^{eff} - P_{ab,i}(ai;ai|bi;bi)$$

with the effective core Hamiltonian defined as follows,

$$H_{aa,i}^{eff} = H_{aa,i} + \sum_{j=1}^{N}\sum_{m=1}^{M_j} P_{mm,j}(ai;ai|mj;mj) + \sum_{k=1}^{N}{}_T\sum_{m=1}^{M_k} P_{mm,k}(ai;ai|mk;mk)$$

$$H_{ab,i}^{eff} = H_{ab,i}$$

where $(ai;bi|mj;nj) = \int\int dv_1 dv_2 h_{ai}(1) h_{bi}(1) r_{21}^{-1} h_{mj}(2) h_{nj}(2)$

The first and second terms stand for the interaction between electrons of the i-th bond and those for other bonds within the inner (I, D or C) and outer (T) regions, respectively. The last sum comes from region T, containing N bonds and is an additive constant.

Once we have optimized all parameters of the SLMO, the molecular orbitals for region C can be expanded on this basis set and a secular equation can be written for the derivation of expansion coefficients. Its dimensionality is determined by the size of region C alone. The molecular orbitals can be written as $\psi_m^C = \sum_{k=1}^{M_C} a_{mk}\phi_k$, where ϕ_k stands for the two-centre SLMO obtained from the solution of equation $F_i C_{mi} = \epsilon_{mi} C_{mi}$. We then have to solve the following secular equation $F_{a_m}^C a_m = \epsilon_m^C a_m$ with

$$F_{ij} = H_{ij}^{eff} = \sum_{k,l}^{M_C} P_{kl}\{(ij|kl) - \tfrac{1}{2}(ik|jl)\}$$

$$H_{ij}^{eff} = H_{ij} + 2 \sum_{k \epsilon D,I,T} (ij|kk)$$

h) various other group function techniques are used, for example, for performing molecular electronic structure calculations using electronic wavefunctions which make explicit reference only to valence electrons, making use of projection operators to project out the core function space from the valence electron wavefunction, and which can be used in conjunction with any desired treatment of the valence electron wavefunctions. The energy calculated is guaranteed to converge, with increasing size of orbital basis, upon the valence energy which would be obtained from an equivalent all-electron calculation using a frozen SCF description of the core electrons. This method is particularly efficient for molecules involving heavier atoms than those of first or second row of the Periodic Table.

For the description of the whole system a mixed quantum/classical methodology can be used [2b], wherein only those atoms directly involved in the chemical process are treated quantum mechanically and the remainder are treated as classical particles.

The system is partitioned into three parts: a quantum mechanical region, a classical or molecular mechanics region, and a boundary region. The quantum and classical regions contain the atoms that are explicitly treated in the calculation. The boundary region accounts for the surroundings that are otherwise neglected.

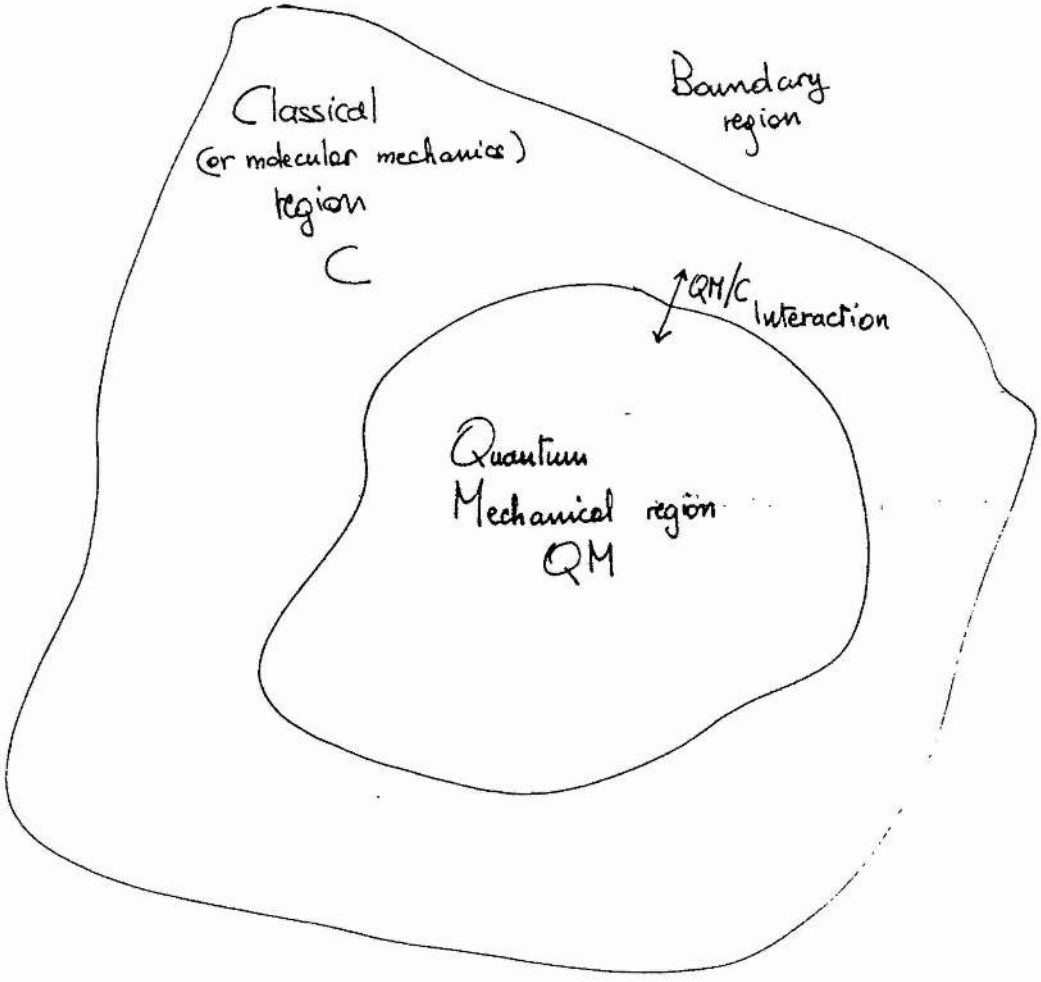


Fig. I.4.1

The solution of the time-independent Schrödinger equation for the electronic wavefunction of the quantum region Ψ, is constructed from the effective hamiltonian of the system, $\hat{H}_{eff}$,

$$\hat{H}_{eff}\Psi(\mathbf{r}, R_Q, R_C) = E\Psi(\mathbf{r}, R_Q, R_C) \tag{I.4.1}$$

The wavefunction, Ψ depends explicitly on the coordinates of electrons, $\mathbf{r}$, and it depends on the position of the quantum mechanical nuclei, R_Q, and the classical region atoms, R_C, in a parametric manner. For each geometry of the nuclei and the classical region atoms the energy is given as the expectation value of $\hat{H}_{eff}$

$$E = \frac{<\Psi|\hat{H}_{eff}|\Psi>}{<\Psi|\Psi>} \tag{I.4.2}$$

To achieve the partitioning illustrated in Fig I.4.1 the effective hamiltonian for the system is written as the sum of four terms

$$\hat{H}_{eff} = \hat{H}_{QM} + \hat{H}_C + \hat{H}_{QM/C} + \hat{H}_{bound} \tag{I.4.3}$$

and the total energy is the sum of the expectation values of each term in the Hamiltonian, i.e.,

$$E_{eff} = E_{QM} + E_C + E_{QM/C} + E_{bound} \tag{I.4.4}$$

the first term in Eq.(I.4.3) is the Hamiltonian describing the quantum mechanical particles (electrons and nuclei) of the system and their interactions with each other. The classical part of the Hamiltonian, H_C, describes the classical region and is analogous to that described in Eq.(I.2.1). $\hat{H}_{QM/C}$ describes the interaction between the quantum fragment and classical atoms and $\hat{H}_{bound}$ can be separated into $\hat{H}_{bound/QM}$, describing the interactions of the quantum fragment with the boundary regions $\hat{H}_{bound/C}$ describing the interactions between the classical and the boundary

region. Since the wavefunction depends only parametrically on the Rc, the terms E_C and $E_{bound/C}$ can be taken outside the integral in Eq.(I.4.2) giving

$$\frac{<\Psi|\hat{H}_{QM}+\hat{H}_{QM/C}+\hat{H}_{bound/QM}|\Psi>}{<\Psi|\Psi>}+E_C+E_{bound/C}$$

.

The quantum fragment is described using one of the previously mentioned fragment methods, for example the Group Function Approach that will be extensively illustrated in the II Part of this thesis. Whatever the method used, one is faced with the problem of proper treatment of the junction region between the monomeric units. For example, in the context of using localized orbitals as building blocks we are faced with the problem of what to do with the nuclei. It is a common procedure to consider a certain portion of the nuclear charge to belong to the bond forming electrically neutral subunits. It is needless to say that such a prescription is quite arbitrary [76]. The prototype molecule approach to the quantum chemical treatment of extended systems has proved to be a valuable tool, especially if the chemical phenomenon of interest is mainly of local character. The prototype molecules are formed by saturating the broken bonds by some appropriately selected atoms. In the context of semi-empirical procedures several attempts have been made to use "pseudoatoms" which mimic the hybridization and electronegativity of the usually polyvalent atom at the frontier of the cluster. Another possibility is to saturate dangling bonds of the representative cluster with hydrogen atoms [77-79].

$<\Psi|\hat{H}_{bound/QM}|\Psi>$ can be calculated by finding an appropriate potential $\hat{H}_{bound/QM}$ representing the electrostatic potential at the relevant fragment site, created by the boundary region.

$E_{bound/C}$ is a completely classical additive contribution.

$\hat{H}_{QM/C}$ consists of two parts if the quantum and classical regions must be treated explicitly:

$$\hat{H}_{QM/C} = V_{QM} + V_C$$

V_{QM} is the electrostatic potential at the relevant fragment site, created by the classical region; it can probably be expanded in an analytic way in function of the features of the classical region and the contribution $< \Psi | V_{QM} | \Psi >$ can therefore be calculated.

V_C is the electrostatic potential created in the space around the quantum fragment by its electrons and nuclei. It is well represented by $V(\mathbf{r})$ of Eq.(I.1.5). The charge distribution $\rho_e(\mathbf{r})$ can be expressed in term of point charges associated with atoms or in terms of multipoles.

Again it must be stressed that the definition of atomic charges, corresponding to a given molecular charge density distribution, is not unique. Numerous population analysis scheme have been proposed, usually in order to improve the classical Mulliken population [4] analysis. In spite of its failure in some cases, the Mulliken charges remain quite popular. Recently it has been shown that the Mulliken population analysis has a privileged role in the LCAO model: this charge distribution has an associated operator. A class of improved population analysis schemes has been designed to reproduce the total dipole moment of the molecule when calculated by point charges. Such a "dipole moment conserving" procedure was proposed e.g. by Jug and by Thole and van Duijnen [80]. A more general multipole fitted scheme has also been derived. Tomasi and coworkers considered the localized two electron bonds as directly transferable from one molecule to another. Model calculations on simple molecules with subsequent localization lead to a library of the charge distributions of the various fragments corresponding to either specific bonds or small functional groups [81]. Alberte Pullman and her coworkers did the first large/scale studies on biological macromolecules, namely on nucleic acids, in the seventies. According to their method, one divides the macromolecule into appropriate subunits and determines the charge distribution of these fragments by fairly good ab initio calculations. Since the

full ab initio evaluation of all electrostatic integrals needed for the determination of the potential would be extremely long, further approximations are necessary to speed up the calculations. Pullman and coworkers used the overlap multipole (OMTP) approximation, which replaces the contribution of each atomic orbital product by a multipole expansion of the potential up to quadrupoles [82].

PART II

THE GROUP FUNCTION

APPROACH

II.1 The Group Function Approach: Historical Background.

In the Group Function Approach the subsystems are various localized electronic groups e.g. atomic core, lone pairs, covalent bonds into which the molecule is formally divided [83-88]. This approach uses Generalized Product Functions to describe various weakly interacting electronic groups. The electronic wavefunction of a molecule is written as an antisymmetrized product of factors (one for each electronic 'group'):

$$\Psi = \hat{A}[\Phi_a^A \Phi_b^B .....] \qquad (II.1.1a)$$

where Φ_a^A, for example, describes 'group A' in a given 'state a'.

It is normally assumed that the group functions Φ_r^R are individually antisymmetric. In this case,

$$\hat{A} = \sum_T \epsilon_T T \qquad (II.1.1b)$$

where T is a transposition (or multiple transposition) which exchange variables between different groups: $\epsilon = \pm 1$.

The wavefunction of each electronic group in the field of the other is optimized using an iterative method to obtain a 'self-consistent group function'.

The Group Function Approach was firstly considered by Hurley, Lennard-Jones and Pople [83], using two electron functions as group functions, in their formulation of VB theory. Parks and Parr generalized the approach in a formal way [85,86] and Parr

and Lykos extended the method to groups with any number of electrons (Generalized Antisymmetric Product Wavefunction) [84]. Different electron groups were supposed to be strongly orthogonal in the sense

$$\int \Psi_r^R(1,i,j,...)\Psi_s^S(1,k,l,...)d\mathrm{x}_1 = 0 \qquad \forall R \neq S \tag{II.1.2}$$

This condition is a mathematical formulation of the physical individuality of the different electron groups. Its first application was to the pi-electron system as a group of electrons separated from the sigma core, giving a rigorous justification of the $\sigma - \pi$ separation assumed, for example in Hückel theory. McWeeny extended the analysis from the standpoint of density matrix theory [87,88] giving the explicit form of the operators defining the effective field for each group. We will sketch the lines of the method following this formulation.

Let Ψ_k be a normalized general Product Function corresponding to a particular assignment of states to the various electron groups,

$$\Psi_k = M_k \hat{A}[\Phi_a^A \Phi_b^B .....], \quad k = Aa, Bb, ...$$

When the Strong Orthogonality condition is assumed, the expression for the matrix elements of the Hamiltonian H can be determined with the same facility as for spin-orbitals (as in Slater's rules). The density (and transition density) matrices for the whole system are thus expressible in terms of those for the component electron groups. If $\rho_1(kk'|\mathrm{x}_1;\mathrm{x}_1')$ and $\rho_2(kk'|\mathrm{x}_1,\mathrm{x}_2;\mathrm{x}_1',\mathrm{x}_2')$ are the transition densities connecting states Ψ_k and $\Psi_{k'}$, there are only three cases to consider,

(i) k' not differing from k in any group,

(ii) k' different from k in one group, say R, and

(iii) k' different from k in two groups, R and S say.

If there are differences in three or more groups the one-and two-electron transition

densities vanish as a result of the strong orthogonality. Explicitly, in these three cases:

(i) $k = k' = (a, b, ..., r, ..., s, ...)$

$$\rho_1(kk'|\mathrm{x}_1;\mathrm{x}'_1) = \sum_R \rho_1^R(rr|\mathrm{x}_1;\mathrm{x}'_1)$$

$$\rho_2(kk'|\mathrm{x}_1,\mathrm{x}_2;\mathrm{x}'_1,\mathrm{x}'_2) = \sum_R \rho_2^R(rr|\mathrm{x}_1,\mathrm{x}_2;\mathrm{x}'_1,\mathrm{x}'_2)+$$

$$+(1-P_{12})\sum_{S\neq R}\rho_1^R(rr|\mathrm{x}_1;\mathrm{x}'_1)\rho_1^S(ss|\mathrm{x}_2;\mathrm{x}'_2)$$

(ii) $k = (a, b, ..., r, ..., s, ...)$, $k' = (a, b, ..., r', ..., s, ...)$

$$\rho_1(kk'|\mathrm{x}_1;\mathrm{x}'_1) = \rho_1^R(rr'|\mathrm{x}_1;\mathrm{x}'_1)$$

$$\rho_2(kk'|\mathrm{x}_1,\mathrm{x}_2;\mathrm{x}'_1,\mathrm{x}'_2) = \rho_2^R(rr'|\mathrm{x}_1,\mathrm{x}_2;\mathrm{x}'_1,\mathrm{x}'_2)+$$

$$+(1-P_{12})\sum_{S\neq R}[\rho_1^R(rr'|\mathrm{x}_1;\mathrm{x}'_1)\rho_1^S(ss|\mathrm{x}_2;\mathrm{x}'_2)+\rho_1^S(ss|\mathrm{x}_1;\mathrm{x}'_1)\rho_1^R(rr'|\mathrm{x}_2;\mathrm{x}'_2)]$$

(iii) $k = (a, b, ..., r, ..., s, ...)$, $k' = (a, b, ..., r', ..., s', ...)$

$$\rho_2(kk'|\mathrm{x}_1,\mathrm{x}_2;\mathrm{x}'_1,\mathrm{x}'_2) =$$

$$= (1-P_{12})\sum_{S\neq R}[\rho_1^R(rr'|\mathrm{x}_1;\mathrm{x}'_1)\rho_1^S(ss'|\mathrm{x}_2;\mathrm{x}'_2)+\rho_1^S(ss'|\mathrm{x}_1;\mathrm{x}'_1)\rho_1^R(rr'|\mathrm{x}_2;\mathrm{x}'_2)]$$

where

$$\rho_1(rr'|\mathrm{x}_1;\mathrm{x}'_1) = N_R\int\Psi_r^R(\mathrm{x}_1,\mathrm{x}_2,...,\mathrm{x}_{N_R})\Psi_r^{R^*}(\mathrm{x}'_1,\mathrm{x}_2,...,\mathrm{x}_{N_R})d\mathrm{x}_2...d\mathrm{x}_{N_R}$$

$$\rho_2(rr'|\mathrm{x}_1,\mathrm{x}_2;\mathrm{x}'_1,\mathrm{x}'_2) =$$

$$= N_R(N_R-1)\int\Psi_r^R(\mathrm{x}_1,\mathrm{x}_2,...,\mathrm{x}_{N_R})\Psi_r^{R^*}(\mathrm{x}'_1,\mathrm{x}'_2,...,\mathrm{x}_{N_R})d\mathrm{x}_3...d\mathrm{x}_{N_R}$$

These expression are valid only for strong orthogonal group functions. The corresponding matrix elements of the Hamiltonian are given by,

(i) $H_{kk} = \sum_R H^R(rr) + \frac{1}{2}\sum_{S\neq R}[J^{RS}(rr,ss) - K^{RS}(rr,ss)]$ (II.1.3a)

(ii) $H_{kk'} = H^R(rr') + \sum_{S\neq R}[J^{RS}(rr',ss) - K^{RS}(rr',ss)]$ (II.1.3b)

(iii) $H_{kk'} = J^{RS}(rr',ss) - K^{RS}(rr',ss)$ (II.1.3c)

where the single-group and inter-group terms are as follows:

$$H^R(rr) = <\Phi_r^R|\hat{H}^R|\Phi_r^R>,\ \hat{H}^R = \sum_{i=1}^{N_R} h(i) + \frac{1}{2}\sum_{i,j=1}^{N_R}{}' g(i,j) \qquad \text{(II.1.4a)}$$

$H^R(rr')$ is the matrix element of a Hamiltonian for the N_R electrons of group R taken between states r and r'.

Both $J^{RS}(rr',ss')$ and $K^{RS}(rr',ss')$ are thus expressed in terms of coulomb and exchange operators, generalizing those that appear in Hartree-Fock theory.

$$J^{RS}(rr',ss') = <\Phi_r^R|\sum_{i=1}^{N_R} J^S(i)|\Phi_r^R>$$

$$J^S(1)\psi(\mathrm{x}_1) = \int g(1,2)\rho_1(ss'|\mathrm{x}_2;\mathrm{x}_2)\psi(\mathrm{x}_1)d\mathrm{x}_2 \qquad \text{(II.1.4b)}$$

$$J^{RS}(rr',ss') = \int g(1,2)\rho_1(ss'|\mathrm{x}_2;\mathrm{x}_2)\rho_1(rr'|\mathrm{x}_1;\mathrm{x}_1)d\mathrm{x}_1 d\mathrm{x}_2$$

$J^{RS}(rr',ss')$ is the electrostatic interaction energy of two charge distribution whose densities are $\rho_1(rr'|\mathrm{x}_1;\mathrm{x}_1')$ and $\rho_1(ss'|\mathrm{x}_2;\mathrm{x}_2')$ respectively, namely transition densities for $r \to r'$ in group R and $s \to s'$ in group S.

$$K^{RS}(rr',ss') = <\Phi_r^R|\sum_{i=1}^{N_R} K^S(i)|\Phi_r^R>$$

$$K^S(1)\psi(\mathrm{x}_1) = \int g(1,2)\rho_1(ss'|\mathrm{x}_1;\mathrm{x}_2)\psi(\mathrm{x}_2)d\mathrm{x}_2 \qquad \text{(II.1.4c)}$$

$$K^{RS}(rr',ss') = \int g(1,2)\rho_1(ss'|\mathrm{x}_1;\mathrm{x}_2')\rho_1(rr'|\mathrm{x}_2;\mathrm{x}_1')d\mathrm{x}_1 d\mathrm{x}_2$$

$K^{RS}(rr',ss')$ is a corresponding exchange contribution.

A Group Function analogue of the HF method is obtained by starting with a single generalized product and seeking a minimum value of the corresponding variational energy expression

$$E = \sum_R H^R(rr) + \sum_{R<S} [J^{RS}(rr,ss) - K^{RS}(rr,ss)] \qquad \text{(II.1.5)}$$

where $J^{RS}(rr,ss)$ and $K^{RS}(rr,ss)$ are the expectation values of that part of the energy of the N_R electrons of group R which arises from interaction (coulomb and exchange, respectively) with the electrons of group S. In general, the energy to be minimized to optimize group R is

$$E^R_{eff} = H^R(rr) + \sum_{R\neq S} [J^{RS}(rr,ss) - K^{RS}(rr,ss)] \qquad \text{(II.1.6)}$$

The optimization of the R-group wavefunction becomes essentially an N_R-electron problem, and this is a great simplification with respect to the direct treatment of the N-electron case. Moreover, individual groups may in principle be described by wave functions of high accuracy taking into account electron correlation within each group.

In general, all the above results are valid only for strong-orthogonal group functions. Strong orthogonality can be ensured by working with an explicitly orthogonal basis. Alternatively projection operators can be applied to non-orthogonal sets in order to obtain strong-orthogonal group functions. Such approaches have a long history [89], but owing to their complexity have not been widely used in actual calculations. In most of the present work we construct disjoint orthogonal sets, at the outset, to satisfy the strong-orthogonal condition.

In practical applications some groups can be held frozen in the iterative procedure. This is the case, for example, in core pseudopotential calculations where the core electron wavefunction, represented by a suitable analytical form, remains fixed and the valence electron wavefunction is optimized in the effective field of the core [90]. Here the fulfillment of the orthogonality constraint is more problematic than in the case of the $\sigma - \pi$ separability: the basis functions belonging to the core and valence regions are not orthogonal by symmetry and their overlap is not negligible. Nevertheless for a proper description one ought to ensure the orthogonality of the

valence electrons to the core region, otherwise the former would collapse into the low-energy regions normally occupied by the core electrons. This problem can be avoided either by working with an explicitly orthogonalized basis (valence orbitals Schmidt orthogonalized to the core [91], or by adding some extra conditions to the variational problem, which take into account the orthogonality requirements. The latter approach has been advocated by Huzinaga and Cantu [92], who introduced the coupling (or screening) operator method for pseudopotentials.

The Group Function Approach has an immediate chemical appeal because it stresses the individuality of different bonds or chemically recognizable entities and it has already been successfully used in ab-initio calculations [93-99], and semi-empirical calculations [100]. In fact [97-101], it was shown by McWeeny, Cook and co-workers that various NDDO integral approximations can be at least partially justified if proper basis sets are employed. This implies hybrid orbitals which exhibit a desired localization. In addition they are (Löwdin) orthogonalized. It appears that the integrals abandoned by NDDO approximation are small indeed if this type of AO's is used. We can conclude that the Group Function Approach incorporates many of the concepts of traditional chemistry and lends itself well to semiempirical developments along rather rigorous lines. Besides it can transcend the limitation of the HF theory because correlation can be easily admitted within each electronic group. Group Functions thus can give a rather accurate description of molecular electronic structure, in principle even for very large molecules, provided the different groups are well localized. The remaining problem is to account for the structure and behaviour of a large molecule in terms of the relatively weak interactions between its constituent parts.

As previously mentioned, the GF Theory has served as the basis for various quantum chemical models and for efficient treatments of the electronic correlation problem in the framework of geminal methods [102]. Its main limitation is the need to partition the basis into mutually orthogonal sets, one for each group, in some a priori way. This limits the accuracy of computed total energy and, unfortunately, the possibility of calculating, for example, conformational energy differences.

II.2 The Group Function Approach: Present Applications.

We first perform some test calculations on the ground state of small molecules formed by atoms of the first row (H - F) using an ab-initio version of the group function method. We start by retaining the strong-orthogonality condition between group functions and proceed along the following lines.

a) Firstly we assume that the description of the atomic inner shells is not effected by changes of state of the valence electrons (this being the 'frozen core approximation') [89] and define a function Φ_{core} for the description of the group of the 1s inner electrons, strong orthogonal to the valence electron wavefunction. This last condition is obtained by orthogonalizing the valence orbitals against the core ones by the Schmidt orthogonalization process. The core contribution E_{core} to the energy can therefore be computed separately . The remaining valence electrons are subjected to an effective potential due to the nuclei and the core electrons.

b) Various electron pairs are recognized from the start, one for each single bond, one for each lone pair, and one for each bond in a multiple bond; and the wavefunction is written as an antisymmetrized product of localized two-electron functions (or 'geminals') ...., one for each pair [91].

c) The Strong-orthogonality condition is satisfied by building different geminals from mutually orthogonal sets of orbitals. These are obtained by performing a Löwdin orthogonalization among the valence orbitals.

d) sp^3 hybrids are constructed for each 'heavy' atom (C, O, N, F) pointing along the bond directions.

e) For each bond group a bonding MO (r_1)

$$r_1 = \frac{1}{\sqrt{2}}(b_1 + b_2) \qquad \text{(II.2.1}a\text{)}$$

and an antibonding MO (r_2) are constructed,

$$r_2 = \frac{1}{\sqrt{2}}(b_1 - b_2) \qquad \text{(II.2.1}b\text{)}$$

where b_1 and b_2 are normalized hybrids on the two bonded atoms respectively or $1s$ orbitals for hydrogen atoms.

A double bond is described by two bent bonds* whose bonding and antibonding MOs are constructed by using normalized hybrid orbitals on the two bonded atoms pointing to two ghost atoms with appropriate positions, symmetric to each other with respect to the plane of the double bond.

A lone pair is described by a single hybrid on an atom, containing two electrons.

f) We form a basis of functions comprising three independent singlet functions for each bond pair R, conveniently collected in a row matrix $\mathbf{\Phi}^R$

$$\mathbf{\Phi}^R = (\phi_1^R \phi_2^R \phi_3^R) \qquad \text{(II.2.2)}$$

where

$$\phi_1^R = \frac{1}{\sqrt{2}}|r_1\alpha r_1\beta| \qquad \text{(II.2.2}a\text{)}$$

---

* Pauling [6] explained double and triple bonds by two tetrahedra sharing a common edge and side, respectively. This leads to a description of multiple bond by single curved bonds, similar to the one used by organic chemists for a long time. For example, Baeyer explained the instability of double bond $C = C$ against two single bonds in terms of a strain energy of the two bonds forming the double bond [103].

$$\phi_2^R = \frac{1}{2}(|r_1\alpha r_2\beta| - |r_1\beta r_2\alpha|) \qquad \text{(II.2.2b)}$$

$$\phi_3^R = \frac{1}{\sqrt{2}}|r_2\alpha r_2\beta| \qquad \text{(II.2.2c)}$$

The geminal is then built as a linear combination of them,

$$\Phi^R = \sum_{i=1}^{3} C_{iR}\phi_i^R = \mathbf{\Phi}^R\mathbf{C}_R \qquad \text{(II.2.3)}$$

where $\mathbf{C}_R$ is the column of CI coefficients for group R.

In this way, by admitting limited CI, electron correlation is admitted to some extent within each group

A lone pair is described by a single determinant.

$$\Phi^R = \frac{1}{\sqrt{2}}|r_1\alpha r_1\beta|$$

g) The wavefunction of each electronic group in the field of the others is optimized using an iterative procedure. In the presence of all other groups the energy to be minimized to optimize the description of group R is,

$$E_{eff}^R = H^R + \sum_{S\neq R}[J^{RS} - K^{RS}] = < \Phi^R|\hat{H}_{eff}^R|\Phi^R > \qquad \text{(II.2.4)}$$

where $\hat{H}_{eff}^R = \hat{H}^R + \sum_{S\neq R}[\hat{J}^S - \hat{K}^S]$

$\hat{H}^R = h(1) + h(2) + g(1,2)$

$\hat{J}^S = \hat{J}^S(1) + \hat{J}^S(2)$

$\hat{K}^S = \hat{K}^S(1) + \hat{K}^S(2)$

$\hat{J}^S(1)\psi(\mathbf{x}_1) = [\int g(1,2)\rho_1^S(\mathbf{x}_2,\mathbf{x}_2)d\mathbf{x}_2]\psi(\mathbf{x}_1)$

$\hat{K}^S(1)\psi(\mathbf{x}_1) = [\int g(1,2)\rho_1^S(\mathbf{x}_1,\mathbf{x}_2)\psi(\mathbf{x}_2)d\mathbf{x}_2]$

In a basis like the one defined in f), the minimization consists in solving iteratively, for every group, the eigenvalue equation:

$$\mathbf{H}_{eff}^R\mathbf{C}_R = \lambda_R\mathbf{C}_R \qquad \text{(II.2.5)}$$

where $(\mathbf{H}_{eff}^R)_{\mu\nu} =< \phi_\nu^R|\hat{H}_{eff}^R|\phi_\mu^R >$

i.e., $(\mathbf{H}_{eff}^R)_{\mu\nu} = H_{\mu\nu}^R + \sum_{S\neq R}[J_{\mu\nu}^{RS} - K_{\mu\nu}^{RS}]$

$H_{\mu\nu}^R = \int\limits_{\mathbf{x}_1'=\mathbf{x}_1} h(1)\rho_1^R(\mu\nu|\mathbf{x}_1,\mathbf{x}_1')d\mathbf{x}_1 + \frac{1}{2}\int g(1,2)\rho_2^R(\mu\nu|\mathbf{x}_1,\mathbf{x}_2;\mathbf{x}_1,\mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2$

$J_{\mu\nu}^{RS} = \sum\limits_{\sigma,\lambda} C_{\sigma S}C_{\lambda S}^* \int g(1,2)\rho_1^R(\mu\nu|\mathbf{x}_1,\mathbf{x}_1)\rho_1^S(\sigma\lambda|\mathbf{x}_2,\mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2$

$K_{\mu\nu}^{RS} = \sum\limits_{\sigma,\lambda} C_{\sigma S}C_{\lambda S}^* \int g(1,2)\rho_1^R(\mu\nu|\mathbf{x}_2,\mathbf{x}_1)\rho_1^S(\sigma\lambda|\mathbf{x}_1,\mathbf{x}_2)d\mathbf{x}_1 d\mathbf{x}_2$

With our particular choice of the basis, the H-term elements become, after spin integration

$H_{11}^R = 2 < r_1|h|r_1 > +(r_1r_1|r_1r_1)$

$H_{12}^R = H_{21}^R = \sqrt{2} < r_1|h|r_2 > +\sqrt{2}(r_1r_2|r_1r_1)$

$H_{23}^R = H_{32}^R = \sqrt{2} < r_1|h|r_2 > +\sqrt{2}(r_1r_2|r_2r_2)$

$H_{13}^R = H_{31}^R = (r_1r_2|r_1r_2)$

$H_{22}^R =< r_1|h|r_1 > + < r_2|h|r_2 > +(r_1r_1|r_2r_2) + (r_1r_2|r_2r_1)$

$H_{33}^R = 2 < r_2|h|r_2 > +(r_2r_2|r_2r_2)$

The interaction terms become, after spin integration,

$J_{\mu\nu}^{RS} - K_{\mu\nu}^{RS} =$

$$= \sum_{\sigma,\lambda} C_{\sigma S} C^*_{\lambda S} \int_{\substack{\mathbf{r}'_1=\mathbf{r}_1 \\ \mathbf{r}'_2=\mathbf{r}_2}} d\mathbf{r}_1 d\mathbf{r}_2 [p_1^R(\mu\nu|\mathbf{r}_1,\mathbf{r}'_1) p_1^S(\sigma\lambda|\mathbf{r}_2,\mathbf{r}'_2) - \tfrac{1}{2} p_1^R(\mu\nu|\mathbf{r}_2,\mathbf{r}'_1) p_1^S(\sigma\lambda|\mathbf{r}_1,\mathbf{r}'_2)]$$

where, using the real orbitals r_1 and r_2:

$p_1^R(11|\mathbf{r}_1,\mathbf{r}'_1) = 2r_1 r_1$

$p_1^R(12|\mathbf{r}_1,\mathbf{r}'_1) = p_1^R(21|\mathbf{r}_1,\mathbf{r}'_1) = p_1^R(23|\mathbf{r}_1,\mathbf{r}'_1) = p_1^R(32|\mathbf{r}_1,\mathbf{r}'_1) = \sqrt{2} r_1 r_2$

$p_1^R(22|\mathbf{r}_1,\mathbf{r}'_1) = r_1 r_1 + r_2 r_2$

$p_1^R(13|\mathbf{r}_1,\mathbf{r}'_1) = p_1^R(31|\mathbf{r}_1,\mathbf{r}'_1) = 0$

$p_1^R(33|\mathbf{r}_1,\mathbf{r}'_1) = 2r_2 r_2$

h) The optimum 'self-consistent group approximation' is obtained as the result,

$$\Psi = M\hat{A}[\Phi_A \Phi_B ...]$$

where the transposition in the antysimmetrized Â exchange variables between different groups, and the corresponding valence electron energy is

$$E_{val} = \sum_R H^R + \frac{1}{2} \sum_{S \neq R} [J^{RS} - K^{RS}] \qquad \text{(II.2.6)}$$

The total electronic energy is

$$E = E_{core} + E_{val} \qquad \text{(II.2.7)}$$

all the core-valence interaction terms being included in E_{val}.

II.3 Possibility of Including Non-orthogonality Effects.

The use of 'strong-orthogonal' group functions may sometimes be inadequate to predict barrier heights and other conformational properties because different groups are not allowed to interact, i.e., their wavefunctions do not describe overlapping. Conformational energy differences – of paramount importance in biochemistry and biology – are an exceedingly small fraction of the total electronic energy; and their dependence on molecular geometry depends critically on small *non-orthogonality effects* in the regions where different groups overlap.

Two main approaches to the inclusion of non-orthogonality effects can be explored: (i) the direct use of non-orthogonal group functions with non-orthogonality introduced as a *correction* to the initial approximation; and (ii) the use of *orthogonal* groups, as in the original formulation, but with the addition of 'charge transfer' terms in the wavefunction. These two approaches are clearly related. For example if r and s (non-orthogonal) are in different groups they can be orthogonalized:

$$\bar{r} = r - \lambda s$$

$$\bar{s} = s - \lambda r$$

or (not normalized):

$$r = \bar{r} - \mu \bar{s}$$

$$s = \bar{s} - \mu \bar{r}$$

Any product rs, in a determinant of non-orthogonal orbitals, is thus a linear combination of $\bar{r}\bar{s}$, $\bar{r}\bar{r}$ and $\bar{s}\bar{s}$; and the latter correspond to electron transfer configu-

rations in a formulation based on orthogonalized orbitals. In other words, at a certain level of approximation, the two approaches are essentially equivalent.

We explore the first approach in some detail. We have tried to remove the strong-orthogonality constraint by performing the energy calculation with non-orthogonal group functions in the same way as if they were strong-orthogonal to each other (obtaining the value E_0) and adding the intergroup corrections (for lack of orthogonality) between two groups at a time (E_{cor}^{AB})

$$E_{tot} = E_0 + \sum_A \sum_{B<A} E_{cor}^{AB} \tag{II.3.1}$$

where E_{cor}^{AB} is the correction to the energy for the groups A and B.

The basis for this possibility is found by expanding the wavefunction (Φ) in terms of 0,1,2,... transpositions

$$\Phi = M\hat{A}[\Phi_a^A \Phi_b^B ...] \tag{II.3.2}$$

where M is the normalization factor and $\hat{A} = \sum \epsilon_T T$, T being a transposition between different groups, explicitely,

$$\hat{A} = 1 + \sum_R \sum_{P<R} (- \sum_{i_R, j_P} (i_R, j_P) + \sum_{i_R, i'_R, j_P, j'_P} (i_R, j_P)(i'_R, j'_P) - ...)$$

Up to single interchange terms,

$$E = \frac{< \Phi | H | \Phi >}{< \Phi | \Phi >} =$$

$$= \frac{< \hat{A}[\Phi_a^A \Phi_b^B ...] | H | \hat{A}[\Phi_a^A \Phi_b^B ...] >}{< \hat{A}[\Phi_a^A \Phi_b^B ...] | \hat{A}[\Phi_a^A \Phi_b^B ...] >} =$$

$$= \frac{< \Phi_a^A \Phi_b^B ... | H | \hat{A}[\Phi_a^A \Phi_b^B ...] >}{< \Phi_a^A \Phi_b^B ... | \hat{A}[\Phi_a^A \Phi_b^B ...] >} =$$

$$= \frac{< \Phi_a^A \Phi_b^B ... | H | [1 - \sum_R \sum_{P<R} \sum_{i_R, j_P} (i_R, j_P)] \Phi_a^A \Phi_b^B ... \Phi_p^P ... \Phi_r^R ... >}{< \Phi_a^A \Phi_b^B ... | [1 - \sum_R \sum_{P<R} \sum_{i_R, j_P} (i_R, j_P)] \Phi_a^A \Phi_b^B ... \Phi_p^P ... \Phi_r^R ... >}$$

$$< \Phi | \Phi > = < \Phi_a^A \Phi_b^B ... | \Phi_a^A \Phi_b^B ... > +$$

$$- \sum_R \sum_{P<R} < \Phi_a^A \Phi_b^B ... \Phi_p^P ... \Phi_r^R ... | \sum_{i_R, j_P} (i_R, j_P) | \Phi_a^A \Phi_b^B ... \Phi_p^P ... \Phi_r^R ... >$$

In every term of the summation the overlap between the two groups P and R only is considered different from zero; the overlap between two other groups or between P or R and other groups is neglected.

$$< \Phi | \Phi > = 1 - \frac{1}{4} \sum_R \sum_{P<R} < |p\bar{p}||r\bar{r}|| \sum_{i_R, j_P} (i_R, j_P) ||p\bar{p}||r\bar{r}| > =$$

$$= 1 - \sum_R \sum_{P<R} < pprr | 2pprr > = 1 - \sum_R \sum_{P<R} 2S_{rp}^2$$

$$E = \frac{1}{1 - \sum_R \sum_{P<R} 2S_{rp}^2} \{ < \Phi_a^A \Phi_b^B ... | H | \Phi_a^A \Phi_b^B ... > +$$

$$- \sum_R \sum_{P<R} < \Phi_a^A \Phi_b^B ... \Phi_p^P ... \Phi_r^R ... | \sum_{i_R, j_P} (i_R, j_P) | \Phi_a^A \Phi_b^B ... \Phi_p^P ... \Phi_r^R ... > \}$$

Defining $H = \sum H^Q$, where

$$H^Q = \sum_{i_Q} h_{i_Q} + \frac{1}{2} \sum_{i_Q, j_Q}' g(i_Q, j_Q) + \frac{1}{2} \sum_{S \neq Q} \sum_{i_Q, j_S} g(i_Q, j_S)$$

then it results,

$$E = \frac{1}{1 - \sum_R \sum_{P<R} 2S_{rp}^2} \{ < \Phi_a^A \Phi_b^B ... | \sum_Q H^Q | \Phi_a^A \Phi_b^B ... > +$$

$$- \sum_R \sum_{P<R} (\sum_{Q \neq R,P} E_0^Q < \Phi_p^P \Phi_r^R | \sum_{i_R, j_P} (i_R, j_P) | \Phi_p^P \Phi_r^R > +$$

$$< \Phi_p^P \Phi_r^R | H^P + H^R | \sum_{i_R, j_P} (i_R, j_P) \Phi_p^P \Phi_r^R >)$$

$$E = < \Phi_a^A \Phi_b^B ... | H | \Phi_a^A \Phi_b^B ... > - < \Phi_a^A \Phi_b^B ... | H | \Phi_a^A \Phi_b^B ... > +$$

$$+ \frac{1}{1 - \sum_R \sum_{P<R} 2S_{rp}^2} \{ < \Phi_a^A \Phi_b^B ... | H | \Phi_a^A \Phi_b^B ... > +$$

$$- \sum_R \sum_{P<R} [(\sum_{Q \neq R,P} (E_0^Q \dot{2} S_{rp}^2) + < pprr | H^P + H^R | 2prrp >] \} =$$

$$= < \Phi_a^A \Phi_b^B ... | H | \Phi_a^A \Phi_b^B ... > +$$

$$+ \frac{1}{1 - \sum_R \sum_{P<R} 2S_{rp}^2} \{ < \Phi_a^A \Phi_b^B ... | \sum_Q H^Q | \Phi_a^A \Phi_b^B ... > (1 - 1 + \sum_R \sum_{P<R} 2S_{rp}^2) +$$

$$- \sum_R \sum_{P<R} \sum_{Q \neq R,P} 2S_{rp}^2 E_0^Q - \sum_R \sum_{P<R} 2 < pprr | H^P + H^R | prrp > \} =$$

$$= < \Phi_a^A \Phi_b^B ... | H | \Phi_a^A \Phi_b^B ... > + \frac{1}{1 - \sum_R \sum_{P<R} 2S_{rp}^2} \{ \sum_R \sum_{P<R} 2S_{rp}^2 < \Phi_a^A \Phi_b^B ... | \sum_Q H^Q | \Phi_a^A \Phi_b^B ... >$$

$$-\sum_R \sum_{P<R} \sum_{Q\neq P,R} 2S_{rp}^2 E_0^Q - \sum_R \sum_{P<R} 2 < pprr|H^P + H^R|prrp > \} =$$

$$=< \Phi_a^A \Phi_b^B ...|H|\Phi_a^A \Phi_b^B ... > +$$

$$+\frac{1}{1-\sum_R \sum_{P<R} 2S_{rp}^2} \sum_R \sum_{P<R} \{2S_{rp}^2 < \Phi_p^P \Phi_r^R|H^P+H^R|\Phi_p^P \Phi_r^R > -2 < pprr|H^P+H^R|prrp >\}$$

$$=< \Phi_a^A \Phi_b^B ...|H|\Phi_a^A \Phi_b^B ... > +$$

$$+\frac{1}{1-\sum_R \sum_{P<R} 2S_{rp}^2} \sum_R \sum_{P<R} \{2S_{rp}^2 < pprr|H^P+H^R|pprr > -2 < pprr|H^P+H^R|prrp >\}$$

This calculation suggests that the energy can be computed as the sum of zero transposition term and a number of contributions $E^{AB}(S_{ab})$ one for each pair of groups. We will calculate one such contribution reasoning as if the system would consist of the two groups in question only.

$$E^{AB}(S_{ab}) = \frac{1}{1-2S_{ab}^2}\{2S_{ab}^2 < bbaa|H^B + H^A|bbaa > -2 < bbaa|H^B + H^A|baab >\} =$$

$$= \frac{1}{1-2S_{ab}^2}\{2S_{ab}^2(2h_{aa} + 2h_{bb} + < aa|g|aa > + < bb|g|bb > +4 < ab|g|ba >) +$$

$$-2(h_{bb}S_{ab}^2 + h_{aa}S_{ab}^2 + 2h_{ab}S_{ab} + (< bb|g|ba > + < aa|g|ab >)S_{ab} +$$

$$-4h_{ab}S_{ab} - 4(< bb|g|ba > + < aa|g|ab >)S_{ab} + 6 < ba|g|ba > S_{ab}^2\}+$$

$$+\frac{1}{1-2S_{ab}^2}\{[2(1-2S_{ab}^2)-2] < ba|g|ab >\} =$$

$$= E_{pen}^{AB} + E_{exch}^{AB}$$

$$E_{pen}^{AB} = \frac{1}{1-2S_{ab}^2}\{2S_{ab}^2(2h_{aa} + 2h_{bb} + < aa|g|aa > + < bb|g|bb >)+$$

$$-4h_{ab}S_{ab} - 4(< bb|g|ba > + < aa|g|ab >)S_{ab} + 6 < ba|g|ba > S_{ab}^2\}$$

$$E_{exch}^{AB} = \frac{-2S_{ab}^2}{1-2S_{ab}^2} < ba|g|ab >$$

Accurate ab initio calculations and a non-orthogonal bond-orbital analysis of the barriers to internal rotation carried out on small molecules, following researches concerning the orientation dependence of intermolecular interactions [104] have shown that non-orthogonality and first-order penetration and exchange effects between electrons belonging to different groups are the most important contributors to these barriers, at least for molecules possessing electron lone pairs on one side of bonds at most and provided rigid rotations are assumed.

The energy can be decomposed in a sum

$$E = E_{cb} + E_{pen} + E_{exch}$$

E_{cb} is the Coulombic component of the energy and includes the energy contributions from individual localized groups plus the Coulombic interactions between different groups.

$E_{pen} = \sum_{A} \sum_{B<A} E_{pen}^{AB}$ is the penetration component of the one-configuration energy associated with the overlap among localized charge distributions and depends strictly upon non-orthogonality of the bond orbitals, as the formula previously developed show.

$E_{exch} = \sum_{A} \sum_{B<A} (E_{exch}^{AB}(S_{ab}) + E_{exch}^{AB}(0))$ is associated with 2-electron exchange between different groups and survives even in the case of no overlap.

Both terms E_{pen} and E_{exch} are non-classical in the sense that they arise as a consequence of the antisymmetry requirements imposed upon the wavefunction by the Pauli principle. For closed shells $E_{pen}(> 0)$ describes repulsion and each $E_{exch}(< 0)$ attraction, and the penetration energy results from the competing effect of these two contributions; E_{exch} is smaller, in absolute value, for bonds but becomes increasingly larger in the presence of lone pairs.

The approximation of the antisymmetrizer up to single interchange terms correspond to the S^2 approximations of exchange and penetration energies. These approximations have been widely used and found largely adequate [105] at least to give qualitative results.

Clearly the inclusion of non-orthogonality corrections, although making little difference to the total electronic energy, makes the calculation vastly more complicated.

II.4 Approximations

The main obstacle to applications on large molecules of biological importance is the calculation of a huge number of two-electron integrals. Some approximations must be introduced. They all are based on the fact that the overlap integral between two localized functions decreases very rapidly outside the localization region; this consideration can be thought of as a definition of localized functions or a measure of the goodness of the localization itself and corresponds to the neglect of small integrals. Two approximations are therefore added to the previously outlined scheme. In step g) only the two-electron integrals within each two neighbouring groups are retained. For groups separated by at least one bond the exchange integrals are neglected and the coulomb integrals are approximated as the inverse of the distance between the centroids of the two bonds involved. The grounds for neglecting small terms have been examined in considerable detail; from the theoretical point of view in Section II.5; this has involved the definition and approximation of the 'effective field' for each electronic group in the whole molecular environment. Numerical evaluations of the neglected terms are presented in Section II.6.1 using hydrocarbon chains as model systems.

II.5 The 'effective field'

It is a matter of some philosophical interest to regard the molecule as a set of (weakly interacting) chemical groups because it represents the picture of molecules seen primarily from the chemical point of view. Once the mathematical description of the isolated group has been established, molecular properties can be calculated in terms of group contributions and intergroup interactions. We can accept the concept of a chemical group, for example a bond, as an empirical fact [106]. A very different approach has been followed by Bader [107] who shows that a molecule can be represented as a set of deformed atoms, separated by certain zero-flux boundaries. In this theory the total energy is a sum of atomic contributions and there are no terms representing bond energies; to obtain a theoretical definition of electron pairs, and consequently of the bond, he uses the negative of the Laplacian of the charge density $\nabla^2\rho = (\frac{\partial^2\rho}{\partial x^2} + \frac{\partial^2\rho}{\partial y^2} + \frac{\partial^2\rho}{\partial z^2})$. A negative value of the Laplacian determines where the density is locally compressed; a positive value where it is locally expanded. He found that the places where the electronic charge is compressed mimic electron pairs.

We would like to define a group as a chemical entity which can be ideally extracted from the context. In particular we can define a bond as a group formed by (i) two valence electrons and (ii) fractions of the nuclei and core electrons of the two atoms connected to each other. A lone pair is a group formed by (i) two valence electrons and (ii) fractions of the nucleus and core electrons of the atom possessing the lone pair. Distant groups can be seen as neutral. In fact, for a chemical group defined in this way an (approximate) effective hamiltonian can be defined which is affected only from its neighbouring groups, relevant because of the exchange interactions.

According to Eqq. (I.3.1.1a) - (I.3.1.c) and Eqq. (II.1.4a) - (II.1.4c) the full hamiltonian for an N-electron system is

$$\hat{H} = \sum_{i=1}^{N} h(i) + \frac{1}{2} \sum_{i,j=1}^{N} {}' g(i,j) \tag{II.4.1}$$

In the frozen core approximation a valence hamiltonian is defined

$$\hat{H}_V = \sum_{i=1}^{N_V} h_{val}(i) + \frac{1}{2} \sum_{i,j=1}^{N_V} {}' g(i,j) \tag{II.4.2a}$$

$$h_{val}(i) = h(i) + (J^C(i) - K^C(i)) =$$

$$= -\frac{1}{2}\nabla^2(i) - \sum_k \frac{Z_k}{r_{ki}} + J^C(i) - K^C(i) = -\frac{1}{2}\nabla^2(i) + V(i) \tag{II.4.2b}$$

where h is the hamiltonian for an electron in the field of the bare nuclei; J^C and K^C are the Coulomb and exchange operators for the core respectively; thus $V(i)$ is the effective field due to nuclear charges and core electrons. For an electron i, the core of an atom k at large distance, consisting in a nucleus and two core electrons, assumes point charge form with Z_k^{val} = number of valence electrons provided by atom k.

The group R hamiltonian becomes

$$\hat{H}_R = \sum_{i=1}^{N_R} [h_{val}(i) + \sum_{S \neq R} (J^S(i) - K^S(i))] + \sum_{i,j=1}^{N_R} {}' g(i,j).$$

Problem is how to write matrix elements

$$< \chi_r | V + \sum_{S \neq R} (J^S - K^S) | \chi_{r'} >$$

so that contributions from distant groups are negligible.

For this purpose it is convenient (though arbitrary) to divide Z_k^{val}, nucleus k assumed to be in group R, into terms $Z_{S_k}^{val}$, where S is another group containing k: then $\sum_{T\epsilon k} Z_{T_k}^{val} = Z_k^{val}$. A partition of $V(i)$ can be obtained following the same lines, such that $\sum_R \hat{V}_R(i) = V(i)$: the part of $\hat{V}_R(i)$ arising from the core of the atom n is built by dividing $V_n(i)$, arising from the whole nucleus n, into a number of equivalent parts, one for each valence electron; δ_n^R such parts contribute to group R. Thus $\hat{V}_R(i) = \sum_{n\epsilon R} \hat{V}_n(i)\frac{\delta_n^R}{n_{Rn}}$ where n_{Rn} is the number of valence electron contributed by atom n.

For a two electron group

$$\hat{V}_S = \hat{V}_{S_1}\frac{\delta_1^S}{n_{S1}} + \hat{V}_{S_2}\frac{\delta_2^S}{n_{S2}}$$

$$\delta_1^S = \begin{cases} 1 & \text{if S is a bond,} \\ 2 & \text{if S is a lone pair.} \end{cases}$$

$$\delta_2^S = 2 - \delta_1^S$$

The global R-group hamiltonian consists in a term depending only on R-group nuclei and electrons and in a series of interaction terms each one contributed by the nuclei and electrons belonging to a single group S.

$$\hat{H}_R = \sum_{i=1}^{N_R}(-\frac{1}{2}\nabla^2(i) + V_R(i)) + \frac{1}{2}\sum_{i,j=1}^{N_R}{}'g(i,j) + \sum_{S\neq R}[\sum_{i=1}^{N_R}(J^S(i) - K^S(i) + V_S(i))]$$

Problem is reduced to write matrix elements

$$< \chi_r | J^S - K^S + V_S | \chi'_r >$$

which can be neglected if R and S are distant groups.

For R and S distant, K^S can be neglected and J^S replaced by a point charge: but the part of $h_{val}(i)$ arising from the core of atom n is $-\frac{Z_n^{val}}{r_{ni}}$ so the part arising from all nuclei in group S will be $-\sum_{n\epsilon S}\frac{Z_n^{val}}{r_{ni}} = -\sum_{n\epsilon S}\frac{Z_n^{val}}{R_{Si}}$, where R_{Si} is the distance from the centroid of group S to electron i.

For two-electron groups, the sum of the number of electrons given to group S by the atoms it contains (i.e. the numerator) is always 2.

It is the clear that, in good approximation, the nuclear attraction term $-\frac{2}{R_{Si}}$ and the Coulomb repulsion term J^S will cancel, for J^S in the Coulomb repulsion arising from 2 electrons distributed with density P_S, and $\mathbf{r}_i$ are given a mean value in the integration $\int \chi_r*(\mathbf{r}_i)(\frac{1}{R_{Si}})\chi'_r(\mathbf{r}_i) = \frac{1}{R_{RS}}$ where R_{RS} is the distance between centroids of groups R and S.

$$< \chi_r|J^S|\chi'_r >= \int \chi_r^*(\mathbf{r}_i)\chi'_r(\mathbf{r}_i)\frac{1}{r_{ij}}P_S(\mathbf{r}_j)d\mathbf{r}_i d\mathbf{r}_j =$$

$$= \int \chi_r^*(\mathbf{r}_i)\chi'_r(\mathbf{r}_i)\frac{1}{R_{RS_i}}d\mathbf{r}_i \int P_S(\mathbf{r}_j)d\mathbf{r}_j$$

where $\int P_S(\mathbf{r}_j)d\mathbf{r}_j = 2$.

The near cancellation is self-evident.

Of course, this appoximation need be used only for distant groups in large molecules: for adjacent or nearby groups the matrix elements could be calculated as in a normal ab initio calculation.

A matrix element contribution becomes

$$< \chi_r|\sum_{i=1}^{N_R}(-\frac{1}{2}\nabla^2(i) + V_R(i)) + \frac{1}{2}\sum_{i,j=1}^{N_R}{}'g(i,j) + \sum_{S\neq R}^{vic}[\sum_{i=1}^{N_R}(J^S(i) - K^S(i) + V_S(i))]|\chi'_r >$$

II.6 Results and Discussion

A number of test calculations have been performed on small molecules in their ground states using standard geometries [108] and an STO-3G basis set. The latter has been used because of convenience and speed in calculations. Actually the dependence of the results on the basis set would be an interesting problem to discuss, the localized wavefunction we used being improved by atomic basis sets giving a good description of the "tail" region. This problem is discussed in APPENDIX B.

II.6.1 Saturated Hydrocarbons

The method was first tested on some saturated hydrocarbons. The energy values are collected in Table 1.

Table 1

Energies in Hartrees

molecule	E(HF)	E(APSG)	E(non-orth)
METHANE	-39.7267	-39.7637	-39.7591
ETH-STAG	-78.3055	-78.3388	-78.3512
ETH-ECL	-78.3002	-78.3426	-78.3497
PROP-AA	-116.8851	-116.9097	-116.9338
PROP-AS	-116.8792	-116.9128	-116.9306
PROP-SS	-116.8714	-116.9086	-116.9277
BUT-TRANS	-155.4646	-155.4806	-155.5225
BUT-ECL	-155.4415	-155.4479	-155.4610
BUT-60	-155.4598	-155.4653	-155.5009
BUT-120	-155.4582	-155.4817	-155.5134

It can be noted that a single configuration calculation using group functions gives better results for the ground state energies than the Hartree-Fock method, subject to the limitations due to choice of basis set.

In the case of strong orthogonal group functions, the following rotational barriers are found:

Table 2

molecule	def. of the barrier	ΔE(kJ/m)
ETHANE	Staggered-Eclipsed	+10.0
PROPANE	(Ecl,Gau)-(Ecl,Ecl)	−11.0
PROPANE	(Gau,Gau)-(Ecl,Gau)	+8.14
BUTANE	anti-syn	−85.9

Barriers are not given correctly. For ethane and one calculation on propane they present opposite sign with respect to the corresponding experimental values. Evidently, the orthogonality constraint (which depend on molecular geometry) leads to errors which, although small in absolute terms, are too large to allow a reliable prediction of barrier heights.

On the other hand, when the calculation is corrected for the non-orthogonality of groups, it gives the correct relative stability of the various conformations of the same compounds. The results are collected in Table 3.

Table 3

molecule	def. of the barrier	ΔE(kJ/m)
ETHANE	Staggered-Eclipsed	-3.94
PROPANE	(Ecl,Gau)-(Ecl,Ecl)	-7.61
PROPANE	(Gau,Gau)-(Ecl,Gau)	-8.40
BUTANE	anti-syn	-161.5

The absolute values of the barrier heights are not really useful, and the present calculations, with small basis sets, are only indicative. For example, the corresponding experimental value for Ethane is -12.3kJ/m [109] about four times the calculated value and for butane it is -31kJ/m, about 1/5 of the result of the calculation. It seems, however, that at least qualitatively correct results are obtained when non-orthogonality effects are included.

For the first linear saturated-hydrocarbons, ab initio calculations have been performed to test the goodness of the integral approximations proposed in Sections II.4 and II.5.

In particular, the values of J^{RS}, K^{RS} and V^{RS} for R and S separated by at least one group are collected in Tables 5 to 7 together with the corresponding contributions to the energy of group R. The relative schematic arrangements of bonds are given in Table 4.

Table 4

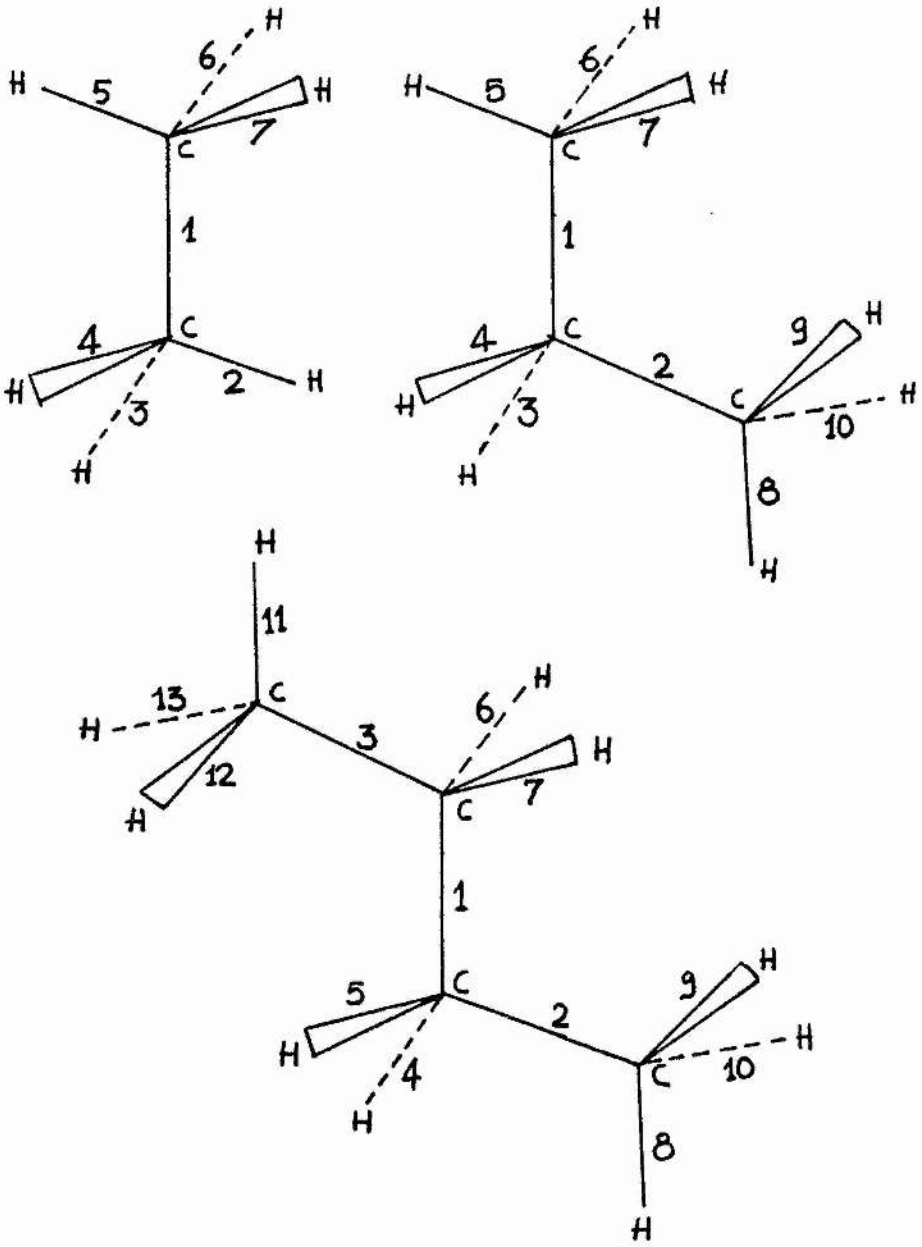

H
6
H
5
H
7
C
1
C
4
2
H
3
H
H
5
6
H
H
7
C
1
C
4
9
H
2
H
3
C
H
10
H
8
H
H
11
C
13
H
6
H
3
H
12
7
H
C
1
C
5
9
H
2
H
C
H
4
10
H
8
H

Table 5

Energies in Hartrees

ETHANE

groups	J(RS)	K(RS)	V(RS)	EN(RS)
(5,2)v	.8448	.0020	-.9253	-.0413
(5,3)v	.9606	.0040	-.9925	-.0180

Table 6

Energies in Hartrees

PROPANE

groups	J(RS)	K(RS)	V(RS)	EN(RS)
(5,2)v	.8477	.0024	-.8784	-.0165
(5,3)v	.9610	.0040	-.9927	-.0178
(6,2)v	.9619	.0036	-.9443	-.0070
(6,4)v	.8452	.0021	-.9253	-.0411
(8,5)o	.5625	.0023	-.5869	-.0183
(8,6)o	.6370	.0001	-.6436	-.0033
(9,6)o	.7470	.0002	-.7588	-.0060
(9,7)o	.8338	.0018	-.8165	-.0077

Table 7

Energies in Hartrees

BUTANE

groups	J(RS)	K(RS)	V(RS)	EN(RS)
(3,2)v	.8507	.0026	-.8808	-.0163
(4,3)v	.9624	.0036	-.9446	-.0071
(6,4)v	.9611	.0040	-.9929	-.0179
(6,5)v	.8455	.0020	-.9258	-.0412
(8,4)v	.9610	.0040	-.9927	-.0178
(9,1)v	.9616	.0036	-.9443	-.0069
(9,4)v	.8451	.0021	-.9253	-.0411
(9,5)v	.9608	.0040	-.9936	-.0184
(8,1)v	.8472	.0024	-.8784	-.0168
(8,3)o	.5638	.0000	-.5739	-.0051
(8,6)o	.6371	.0001	-.6435	-.0032
(9,3)o	.6391	.0001	-.6613	-.0111
(9,6)o	.7472	.0002	-.7589	-.0059
(9,7)o	.8338	.0018	-.8164	-.0078
(11,8)o	.4212	.0000	-.4393	-.0091
(11,9)o	.4659	.0000	-.4685	-.0013
(12,9)o	.5055	.0000	-.5087	-.0016
(12,10)o	.4845	.0000	-.4948	-.0051

A typical calculation of the energy which includes ab initio neighbouring and next neighbouring (due to groups separated by one bond) interaction contributions to the effective field is subjected to an error of about .16% to .28%. If also next neighbouring contributions are neglected the error amounts to about 1.1% to 1.3%. On the other hand, the number of two- electron integrals which must be evaluated in the latter case is smaller than in the previous approximation. In fact, in the calculation of the contribution to the total energy due to group V, the number of two-electron integrals, in the basis of the group functions, is $1 + n^V_{vic}$, where n^V_{vic} is the number of groups vicinal to group V, which are at most 6 if only neighbouring contributions are added, and at most 24 if also the next neighbouring contributions are retained. The number 1 takes into account the V-group two-electron integral, and a factor 2 should multiply n^V_{vic} because one coulomb and one exchange must be calculated for each pair of groups V-W, if a 1/2 factor was not present in the energy expression in order to count the V-W interaction only once.

The total number of two-electrons integrals is $\sum_V^{N_V}(1+n^V_{vic})$, that is, at most, equal to $N_V + 6N_V = 7N_V$ or $N_V + 24N_V = 25N_V$ respectively, when only first row atoms are present.

In a complete calculation, without the approximation introduced in Section II.5, the total number of two-electron integrals is $\sum_V^{N_V}(1 + (N_V - 1)) = N_V^2$.

This difference becomes very important when the number of group increases. Since each group wavefunction is described as a linear combination of two one-electron functions, each coulomb integral involving two group functions depends on 9 different two-electron integrals on the orbital basis and every exchange integral is expansible in terms of 10 of them. Each two-electron integral involving a single group function depends on 6 two-electron integrals. Thus, the total number of different two-electron integrals on the orbital basis is given by

$$\sum_{V}^{N_V}[6 + \frac{1}{2}n_{vic}^{V}(9+10)].$$

The maximum values for this expression are

$$6N_V + \frac{1}{2}\cdot 6\cdot 19N_V = 63N_V$$

or

$$6N_V + \frac{1}{2}\cdot 24\cdot 19N_V = 234N_V$$

respectively.

As a conclusion, we can say that retaining only neighbouring contributions is justified. The inclusion of next neighbouring contributions implies considerable computational costs.

Moreover, we have found that along the series of the hydrocarbons the effective hamiltonian is almost the same for every C-C bond and for every C-H bond, independently of the length of the chain. We will compare these results with others obtained for substituted hydrocarbons for studying the possibility of transferability of H^{eff}.

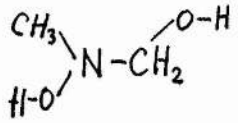
II.6.2 Introducing Double Bonds and Lone Pairs.

In spite of the unusual description of the double bonds as a pair of 'bent' bonds, the group function calculations give results of a similar accuracy. The non-orthogonal group wavefunction energy value is still better than the corresponding HF. For $CH_2 = CH_2$, for example, we find -77.0624 compared with -77.0436 with the HF method.

The values of the energies when lone pairs are present are less accurate:

H_2O: E(HF)=-74.96073; E(non-orth)=-74.91659

NH_3: E(HF)=-55.45254; E(non-orth)=-55.44068



E(HF)=-280.2285; E(non-orth)=-279.5297

Table 8

Energies in Hartrees

molecule	E(HF)	E(GF)	$\Delta\%$
CH3F	-137.1679	-137.1196	.0352
CH2F2	-234.6261	-234.4671	.0678
CHF3	-332.0987	-331.8031	.0890
CF4	-429.5808	-429.1604	.0979

The relative stability of the conformers can still be qualitatively foreseen

H_2O_2 sin : E(HF)=-148.7362; E(non-orth GF)=-148.1927

H_2O_2 anti: E(HF)=-148.7414; E(non-orth GF)=-148.6102.

CH_3OH sin : E(HF)=-113.5455; E(non-orth GF)=-113.5126

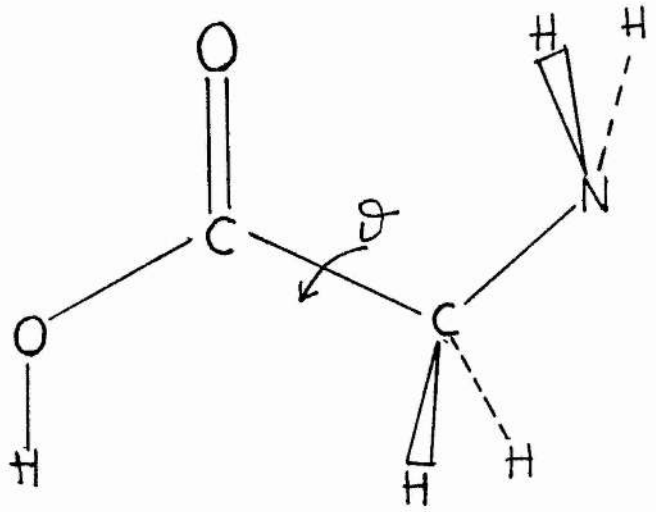
CH_3OH anti: E(HF)=-113.5474; E(non-orth GF)=-113.5132.

The weakness of the model seems to lie in the definition of the lone pairs. It is evident, for example, from the calculation on CH_nF_{4-n}, n=0,1,2,3, that the total energy becomes worse when the number of lone pairs increases. Lone pairs are strictly directed along the bonds; this constraint is probably too strong and should be relaxed in some way.

An element of the effective hamiltonian matrix for C-H group in substituted hydrocarbons differs from the corresponding one for saturated hydrocarbons of a maximum amount of 5%. It is evidently influenced in some way by the presence of more electronegative substituents. The effective hamiltonian for an O-H group is transferable to a good extent.

II.6.3 An Amino Acid

A conformational study of the Glycine has been made, with rotation around the C-C bond through an angle θ



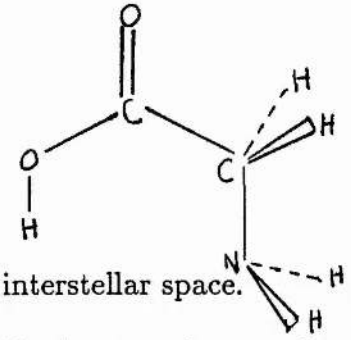
The values obtained are collected in Table 9. According to E(non-orth) it seems that the more stable configuration has θ=90.

Table 9

Energies in Hartrees

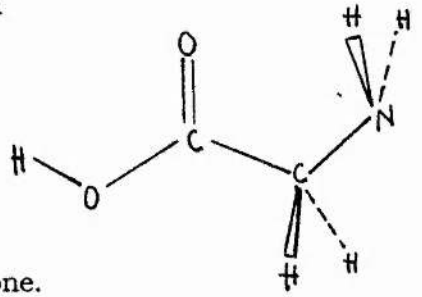
molecule	E(HF)	E(APSG)	E(non-orth)
gly1 ($\theta = 0^o$)	-279.10437	-278.78260	-278.91229
gly5 ($\theta = 60^o$)	-279.10104	-278.78003	-278.92520
gly3 ($\theta = 90^o$)	-279.10019	-278.78026	-278.92905
gly6 ($\theta = 120^o$)	-279.09888	-278.77461	-278.92823
gly4 ($\theta = 180^o$)	-279.09433	-278.75224	-278.91554

Actually experimental evidence was found [110] for the presence of the conformation



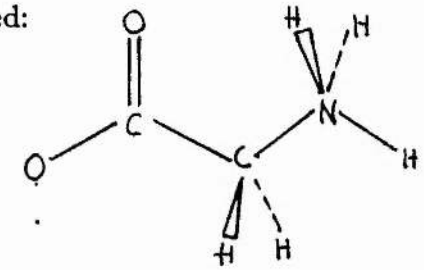
in the vapor of glycine in interstellar space.

RHF results with a 4-31G basis set and a complete geometry optimization [111] give the conformation



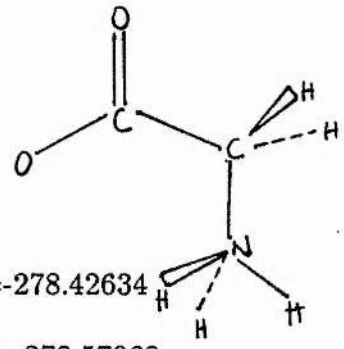
as the favoured one.

The zwitterion system has also been investigated, the following results being obtained:



E(APSG)=-278.40960

E(non-orth)=-278.49906



E(APSG)=-278.42634

E(non-orth)=-278.57068

Comparing these E(non-orth) with the corresponding results for the neutral compounds one finds:

$\Delta E(\theta = 0°) = .4132$

$\Delta E(\theta = 180°) = .3449$

The neutral compound appears to be the more stable.

II.6.4 Conclusions

Summarizing and analysing the results obtained we can conclude that:

a) The Group Function approach uses strictly localized orbitals built from a subset of the atomic orbitals of the molecule whereas the MO SCF approach needs all the basis orbitals for every MO and is thus more accurate (less constrained) for total energy calculations. On the other hand, it is more limited as molecular size goes up because the secular equation to be solved repeatedly has the dimensionality of the basis set. In the Group Function method the complexity of the problem is usually determined by the number of electrons within each group. When, for example, a single determinant of strictly localized orbitals is used for describing a group and these are built from the atomic orbitals (for example hybrid orbitals) centred on the atoms contributing the electrons to the group, the optimization problem is trivial;

b) actually, in the model proposed in this thesis, the localized orbitals are completely determined a priori and do not contain variational parameters; moreover, a group function is constructed by using (locally) excited configurations, other than the ground state configuration, where electrons can occupy a (strictly localized) antibonding orbital, the relative importance of such configurations being determined by a SCF procedure. The contribution to the total energy given by this refinement is not very large, in fact, the mean energy difference for a bond in the two calculations is less than .25%, but it leads to a better description of the group wavefunction and therefore of the electron density; the introduction of this configuration interaction is also important in describing bond breaking because it reduces the importance of the polar structures which in a one determinant ground state description of a two-electron system is overestimated and leads to wrong behaviour on dissociation. The limited CI appears to be unimportant for rotational barriers because it gives an improvement which shows little or no change with molecular conformation;

c) a good prediction of the relative stabilities of the molecular conformations is obtained only when corrections are introduced for taking into account non-orthogonality

effects of the group wavefunctions, as becomes clear from accurate bond orbital calculations on small molecules [112]. These authors show that non-orthogonality and first-order exchange effects (including penetrative and purely exchange contributions) between electron groups, in particular those for vicinal bonds, give the most important contributions to these barriers. As it is evident from the development of section II.3, these exchange energies are strictly dependent on the overlap between group functions. The corresponding barriers resulting from orthogonalized group calculations are usually reversed when non-orthogonality is taken into account.

d) the effective hamiltonian defined in II.5 proves to be very efficient: the interaction terms for distant groups (i.e. for most of the groups in a large molecule) are either negligible or easily estimated. The use of this approximation seems to offer the best method for calculations on very large molecules and this development leads to the same qualitative conclusions as the complete calculation with a great saving of computer time. In fact, the number of two-electron integrals depends linearly on the number of valence orbitals, instead of depending on its fourth power as is the case in a standard SCF calculation with non localized MOs. This introduces an enormous economy when the number of orbitals increases, as in dealing with a very large molecule;

e) the description adopted for the group orbitals gives very good results, in terms of total energies for hydrocarbons, but less good for molecules containig highly polarizable group such as lone pairs. This is quite understandable because in the model proposed every lone pair occupies an sp^3 hybrid orbital with a fixed direction determined by symmetry, which is a very limited description when no optimization is permitted.

f) the unusual description adopted for multiple bonds seems to give good results and introduces a great simplicity in the model, where four hybrids are constructed for each 'heavy' atom dependent only on the geometry of the molecules. The 'bent' bond description has a well established tradition: many accurate ab initio calculations present it as the best description for a certain type of molecules. The present work

suggests that even multiple bonds and traditionally delocalized systems can be well approximated using appropriate bent bond structures;

g) the total energy is formally partitioned in terms of group contributions (Eq. II.1.5). These parts are roughtly transferable from one system to the another one, provided the group environment is not greatly changed.

II.7 PERSPECTIVES

In the many cases where the changes occurring in complex systems such as large molecules, arising for example from reactions or geometry variations, involve only parts of the system, leaving the properties of the rest almost unchanged, the theoretical method presented in this thesis offers a powerful tool for making qualitative predictions. Its main advantage is that it conceptually reduces the system to a series of small fragments (usually bonds or lone pairs) whose description can be optimized considering their interactions with a limited number of vicinal groups, and is therefore very convenient for describing local events

Since the method well represents energy changes resulting from localized effects, such as twisting around a bond, it can be usefully applied to conformational studies and geometry optimization. In such applications it should be possible to use energy differences directly, for relevant fragments, instead of the total energies. This could be a very fruitful field for future development.

The other properties which can be calculated are for the most part directly related to the electron density; this determines, for example, the electrostatic potential outside a molecule and hence the position of attack by approaching ions or polar species. In the GF approximation, the density is simply a sum of densities for all the different groups. Interactions between different molecules are also largely determined by their electron densities a good example being provided by Hydrogen-bonded dimers. Applications of this kind remain to be explored.

Chemical reactions, which involve breaking or re-arrangement of bonds, provide

another vast field of application. Such processes usually involve only localized regions in a molecule and the admission of intragroup CI ensures that the study of bond breaking remains valid throughout the whole process.

The present work points the way to various possible developments in methodology. These include, in particular, the following.

a) Use of the transferability properties of the effective hamiltonian to find better starting group functions in the SCF process and to describe distant groups, so that they do not participate in the optimization process. This would give faster convergence and would reduce the dimensions of the SCF procedure by reducing the optimization to a small fragment of the system.

b) A better description of the lone pairs is also necessary. The total energy in the presence of lone pairs is, in fact, very poorly calculated, even when the sign of the barrier is correctly given. An easily obtained improvement might be obtained by increasing the 2s character of the corresponding hybrid. In fact, as already Pauling suggested, the atoms show a tendency to keep non-bonded electrons, localized in the s orbital, especially when the energy gap $E_p - E_s$ is large: this is because the lone pairs of electrons belong more strongly to the atom than the electrons engaged in bonds. A degree of flexibility in the hybrid lone pair definition could be introduced, simply by defining a further orbital for each lone pair of this type, and allowing it to combine with the fixed hybrid, the coefficients in the linear combination being optimized in exactly the same way as for bonds.

c) When higher accuracy of the total (valence electron) energy is required, the integrals to be calculated accurately include not only those for neighbouring groups but also those between second neighbours; but the cost is high, the number of integrals commonly being increased by a factor of about 4. Similar considerations apply to non-orthogonality corrections. The possibilities of simplification require detailed investigation.

d) A further refinement would be to estimate the terms neglected in the definition

of the approximated effective hamiltonian for a group R, by using a dipole approximation to the density in the evaluation of the matrix elements of the effective field due to distant groups, instead of using the mean value of the distance. This would be important for lone pairs, where the negative charge of two electrons is at the lone pair centroid, while the core-charge of two units has its centroid at the nucleus.

e) A great simplification is the use of fixed group orbitals, without introducing polarity parameters, because accurate calculations on small molecules [113] have shown that their effects on the total energy are fully compensated by the introduction of single-excitation configurations within the individual bonds.

Finally, a word must be said about the computer memory and CPU time needed in GF calculations. Little attention has been paid to this problem in the calculations presented in this thesis because only relatively small molecules have been considered, the primary aim being to test the goodness of the method and approximations, but the question becomes of crucial importance as molecular size goes up. Making the choice of using neither vector nor parallel facilities so that the program can be successfully used even in a laboratory with modest computer resources, for example by organic chemists, the usual programming consideration apply. All the quantities which are used many times during a calculation and those whose computation is difficult and time-consuming must be stored; this makes heavy demand on space. Other quantities are computed directly at the moment they are needed; and this makes demand on speed. Since the GF-SCF procedure is very fast and rapidly convergent and easily handled on a small computer, it remains only to optimize the coding of the preparation of the integrals on the valence basis of the appropriate group orbitals. A provisional version of such a program has been written, for implementing the approximate SCF GF method with non-orthogonality corrections on an IBM PC AT. In terms of computer memory, it is capable of performing calculations with up to 200 two-electron groups. Data on CPU time needed are not yet available, but it is already clear that there are no problems in extending our calculations to molecules of biological interest and that such calculations are within the reach of quite small computers.

APPENDICES

APPENDIX A.

The Hydrogen-like orbitals are obtained by solving the time-independent Schrödinger equation for one electron in the field of one nucleus with charge Z

$$\hat{H}\Psi = E\Psi \tag{A.1}$$

where $\hat{H} = -\frac{1}{2}\nabla^2 - \frac{Z}{r}$ and Z=1 for the hydrogen atom.

Each one-electron wavefunction Ψ is a product of a spatial part ψ and a spin function α or β. Here α and β are the two eigenfunctions of the spin angular momentum defined by

$S_z\alpha = \frac{1}{2}\alpha$

$S_z\beta = -\frac{1}{2}\beta$

They are normalized and mutually orthogonal:

$\int \alpha^*\alpha ds = \int \beta^*\beta ds = 1$

$\int \alpha^*\beta ds = \int \beta^*\alpha ds = 0.$

The Schrödinger equation can be solved without this factor, because the hamiltonian $\hat{H}$ is spinless.

The kinetic energy operator $-\frac{1}{2}\nabla^2$ can be expressed in terms of spherical polar coordinates, r, θ and ϕ, defined as shown in Fig.A.1.

Explicitly,

$x = r \sin\theta \cos\phi$

$y = r \sin\theta \sin\phi$

$z = r \cos\theta$

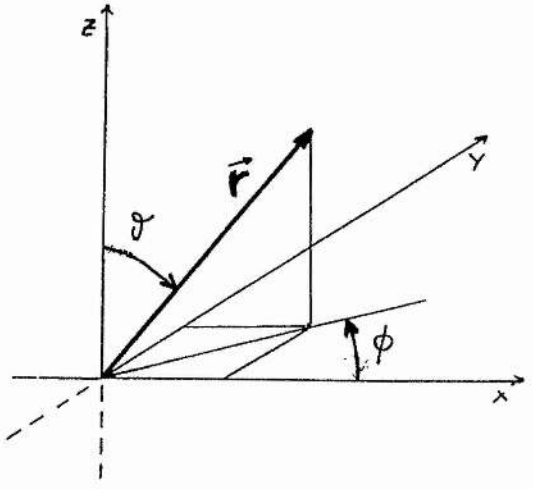


Fig.A.1

Table A.1 - Spherical harmonics

l	m_l	$Y_{lm_l}(\theta, \phi)$
0	0	$1/2\pi^{\frac{1}{2}}$
1	0	$\frac{1}{2}(3/\pi)^{\frac{1}{2}}\cos\theta$
	± 1	$\mp\frac{1}{2}(3/2\pi)^{\frac{1}{2}}\sin\theta e^{\pm i\phi}$
2	0	$\frac{1}{4}(5/\pi)^{\frac{1}{2}}(3\cos^2\theta - 1)$
	± 1	$\mp\frac{1}{2}(15/2\pi)^{\frac{1}{2}}\cos\theta \sin\theta e^{\pm i\phi}$
	± 2	$\frac{1}{4}(15/2\pi)^{\frac{1}{2}}\sin^2\theta e^{\pm 2i\phi}$
3	0	$\frac{1}{4}(7/\pi)^{\frac{1}{2}}(2 - 5\sin^2\theta)\cos\theta$
	± 1	$\mp\frac{1}{8}(21/\pi)^{\frac{1}{2}}(5\cos^2\theta - 1)\sin\theta e^{\pm i\phi}$
	± 2	$\frac{1}{4}(105/2\pi)^{\frac{1}{2}}\cos\theta \sin^2\theta e^{\pm 2i\phi}$
	± 3	$\mp\frac{1}{8}(35/\pi)^{\frac{1}{2}}\sin^3\theta e^{\pm 3i\phi}$

Structure: $Y_{lm_l}(\theta, \phi) = \Theta_{lm_l}(\theta)\Phi_{m_l}(\phi)$

The Scrödinger equation (A.1) becomes

$$-\frac{1}{2r}\frac{\partial^2}{\partial r^2}r\psi - \frac{1}{2r^2}\Lambda^2\psi - \frac{Z}{r}\psi = E\psi \tag{A.2}$$

where

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} \tag{A.3}$$

The Scrödinger equation in this case can be solved by the separation of variables technique, putting $\psi = R(r)Y(\theta,\phi)$,

$$\frac{r\frac{\partial^2}{\partial r^2}[rR(r)]}{R(r)} + \frac{\Lambda^2 Y(\theta,\phi)}{Y(\theta,\phi)} + 2Zr + 2Er^2 = 0$$

giving

$$\begin{cases} \Lambda^2 Y(\theta,\phi) = kY(\theta,\phi) \\ r\frac{\partial^2}{\partial r^2}[rR(r)] + (2Zr + 2Er^2)R(r) = -kR(r) \end{cases}$$

The first equation of the system is the one satisfied by the spherical harmonics $Y_{lm_l}(\theta,\phi)$*

$$\Lambda^2 Y_{lm_l}(\theta,\phi) = -l(l+1)Y_{lm_l}(\theta,\phi) \tag{A.4}$$

where the labels l and m_l are limited to the values $l = 0,1,2,...$ and $m_l = l, l-1, ...0, ..., -(l-1), -l$ (giving $2l+1$ values for a given value of l).

The harmonics themselves consist of two factors, one a function of ϕ alone, the other a function of θ. That is,

* the HANDBOOK OF MATHEMATICAL FUNCTIONS, M.Abramowitz and I.A.Stegun, Dover, is one of the principal sources for identifying solutions of differential equations.

$$Y_{lm_l}(\theta,\phi) = \Theta_{lm_l}(\theta)\Phi_{m_l}(\phi)$$

where $\Phi_{m_l} = \sqrt{\frac{1}{2\pi}}e^{im_l\phi}$ and Θs are standard functions known as the associated Legendre functions

$$\Theta_{lm_l}(\theta) = \{\frac{(2l+1)(l-|m_l|)!}{2(l+|m_l|)!}\}^{\frac{1}{2}} P_l^{|m_l|}(\cos\theta)$$

Here $P_l^{|m_l|}(\cos\theta)$ are the associated Legendre Polynomials, defined by the formulae

$$P_l^{|m_l|}(\cos\theta) = \frac{(l+|m_l|)!}{(l-|m_l|)!2^l l!}\sin^{-m_l}(\theta)[\frac{d^{l-|m_l|}}{(d\cos\theta)^{l-|m_l|}}(\cos^2\theta-1)^l].$$

They are subjected to the orthogonality condition

$$\int_{-1}^{1} P_l^{|m_l'|}(z)P_l^{|m_l|}(z)dz = \begin{cases} \frac{2}{(2l+1)}\frac{(l+|m_l|)!}{(l-|m_l|)!} & \text{for } l \neq l' \\ 0 & \text{for } l=l' \end{cases}$$

The first normalized spherical harmonics $Y_{lm_l}(\theta,\phi)$ are listed in Table A.1.

It is convenient to introduce the real combinations

$$Y^C_{lm_l} = [(-1)^m_l Y_{lm_l} + Y_{l-m_l}]/\sqrt{2}$$

$$Y^S_{lm_l} = -i[(-1)^m Y_{lm_l} - Y_{l-m_l}]/\sqrt{2}$$

in which the $e^{\pm m\phi}$ is replaced by $\sqrt{2}\cos(m_l\phi)$ or $\sqrt{2}\sin(m\phi)$ respectively.

The degeneracy of functions with different m_l values may be exploited in setting up atomic orbitals expressible in terms of cartesian coordinates. These "cubic harmonics" are so frequently preferable in quantum chemistry that we list the first few in Table A.2.

Table A.2 - Cubic harmonics in cartesian form

***s* functions**	$N_s \times 1$			
***p* functions**		p_x	p_y	p_z
	$(N_p/r) \times$	x	y	z
***d* functions**		d_{z^2}	$d_{x^2-y^2}$	
	$(N_d/r_2) \times$	$\frac{1}{2}(3z^2 - r^2)$	$\frac{1}{2}\sqrt{3}\,(x^2 - y^2)$	
		d_{yz}	d_{zx}	d_{xy}
	$(N_d/r^2) \times$	$\sqrt{3}\,yz$	$\sqrt{3}\,zx$	$\sqrt{3}\,xy$
***f* functions**		f_x	f_y	f_z
	$(N_f/r^3) \times$	$\frac{1}{2}(5x^2 - 3r^2)x$	$\frac{1}{2}(5y^2 - 3r^2)y$	$\frac{1}{2}(5z^2 - 3r^2)z$
		f'_x	f'_y	f'_z
	$(N_f/r^3) \times$	$\frac{1}{2}\sqrt{15}\,(y^2 - z^2)x$	$\frac{1}{2}\sqrt{15}\,(z^2 - x^2)y$	$\frac{1}{2}\sqrt{15}\,(x^2 - y^2)z$
		f_{xyz}		
	$(N_f/r^3) \times$	$\sqrt{15}\,xyz$		

Normalizing factors

$$N_s = \frac{1}{2}\left(\frac{1}{\pi}\right)^{1/2} \quad N_p = \frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2} \quad N_d = \frac{1}{2}\left(\frac{5}{\pi}\right)^{1/2} \quad N_f = \frac{1}{2}\left(\frac{7}{\pi}\right)^{1/2}$$

The radial equation becomes,

$$r\frac{\partial^2}{\partial r^2}[rR(r)] + (2Zr + 2Er^2)R(r) - l(l+1)R(r) = 0$$

The radial wave equation is the same as the differential equation in mathematics which has the associated Laguerre function $L_{n+l}^{2l+1}(\rho)$ as acceptable solutions:

$$R_{nl}(r) = -[(2Z/na)^3\{\frac{(n-l+1)!}{2n[(n+l)!]^3}\}]^{\frac{1}{2}}\rho^l L_{n+l}^{2l+1}(\rho)e^{-\rho/2}$$

where $\rho = (\frac{2Z}{na})r$; $a = a_0\frac{m_e}{\mu}$;

$a_0 = 1.529\mathring{A}$, Bohr radius; $\mu = \frac{mm_e}{m+m_e}$, reduced mass.

Laguerre Polynomials are defined as

$$L_{n+l}^{2l+1}(\rho) = (-1)^{(2l+1)}\frac{[(n+l)!]^2}{(2l+1)!(n-l-1)!}e^z\rho^{-(2l+1)}\frac{d^{n-l-1}}{dz^{n-l-1}}(e^{-\rho}z^{n+l})$$

where n is restricted to the values $n = 1, 2, 3, ...$ and the label l can take the values $l = 0, 1, 2, ..., n$. Atomic orbitals are usually named s, p, d, f,... when they take l values $l = 0, 1, 2, 3, ...$ respectively. Atomic orbitals are often described as linear combinations of Slater or Gaussian orbitals, whose radial part is independent of the angular quantum number l.

Slater orbitals are defined as

$$R_n(r) = C_n r^{n-1}e^{-\xi r}, \quad C_n = \frac{(2\xi)^{n+\frac{1}{2}}}{\sqrt{(2n)!}}$$

and Gaussian orbitals are

$$R_n(r) = C_n r^{n-1}e^{-\xi r^2}, \quad C_n = [\frac{2^{2n}(n-1)!}{(2n-1)!}\sqrt{\frac{(2\xi)^{2n+1}}{\pi}}]^{\frac{1}{2}}$$

where ξ is a parameter.

The radial factor may be associated with any harmonic (Table A.1 and A.2).

APPENDIX B.

Perhaps the greatest single problem in the calculation of accurate molecular wavefunctions, and hence of electronic structure and properties, is how to optimize the representation (usually in terms of Gaussian functions) of the atomic orbitals used as a basis for the calculation.

In all work involving weak interactions between molecules (or between weakly overlapping groups in the same molecule) the extent of the overlap between the 'tails' of the wavefunction employed is of crucial importance. Even for single atoms, however, the behaviour of the atomic orbitals at large distance from the nucleus is very poorly represented in most current calculations. In all applications of theory to the prediction of conformations, reaction pathways, etc. (in which different chemical groups approach or separate) it is therefore important to design sets of atomic orbitals (i.e. basis sets) that will accurately represent the atoms in the molecule and expecially in the tail regions.

Two methods of performing this optimization have been considered. They both seek the best representation of an atomic valence state, appropriate to the atom in a molecule, but differ in the optimization techniques employed.

(i) In the first method [114] the atomic orbitals employed in the calculations are optimized by admitting a number of configurations to describe each atomic valence state and minimizing the corresponding energy functional both with respect to the orbital and expansion coefficient variations. (ii) A second method has also been explored [113]: this uses a quadratically convergent Multi Configurational SCF procedure,

the energy functional being expanded in a set of parameters corresponding to the expansion up to higher order than the second in some orbital rotation parameters. The first method has proved to give satisfactory results and convergence with much less effort and implementation difficulties than the second. Thus, we develop it in more details in what follows, also if the basis sets obtained are actually not yet been tested in GF calculations because of their relatively large extension.

A key feature of the calculations required to optimize the atomic orbitals is the division of the atomic electronic system into "shells" (e.g. closed shell, open shell), defined by "orbital sets" (e.g. containing doubly-, singly-, partially occupied and empty orbitals). This is followed by the definition of an effective hamiltonian whose eigenvectors yield the orbitals of the various shells, minimizing the average energy of the given configuration. This effective hamiltonian is built using projection operators for the subspace into which the whole space is partitioned.

Let us consider a two-shell system described by a wavefunction in which n_C electrons are assigned to a first (occupied) shell, containing m_C orbitals, n_0 to a second (occupied) shell, containing m_0 orbitals and m_z to the empty shell. In the usual finite basis (e.g. LCAO) approximation such orbitals are constructed from a common set of, say, m basis function $(\chi_1, \chi_2, ...)$

$$\Phi_C = \chi \mathbf{T}_C$$

$$\Phi_0 = \chi \mathbf{T}_0$$

$$\Phi_Z = \chi \mathbf{T}_Z$$

It has been shown [114] that the average energy of the configuration $|(\Phi)^{n_C}(\Phi)^{n_0}|$ may be expressed in term of the projection operators $(\{\mathbf{R_K}\})$ associated with the various subspaces by defining $\mathbf{R}_K = \mathbf{T}_K \mathbf{T}_K^{\dagger}$ (in a non-orthogonal basis)

$$E_{av} = \nu_1 tr\mathrm{R}_1(\mathrm{h} + \mathrm{G}_1) + \nu_2 tr\mathrm{R}_2(\mathrm{h} + \mathrm{G}_2)$$

where $\mathrm{G}_1 = \mathrm{G}(\nu_1'\mathrm{R}_1) + \mathrm{G}(\nu_2\mathrm{R}_2)$

$\mathrm{G}_2 = \mathrm{G}(\nu_2'\mathrm{R}_2) + \mathrm{G}(\nu_1\mathrm{R}_1)$

$\nu_K = n_K/m_K \qquad , \nu_K' = [2(n_K - 1)]/(2m_K - 1)$:

$\mathrm{G}(\mathrm{R}) = \mathrm{J}(\mathrm{R}) - \mathrm{K}(\mathrm{R})/2$

$[\mathrm{J}(\mathrm{R})]_{\mu\nu} = \sum_{\rho\sigma}(\mathrm{R})_{\sigma\rho} < \chi_\mu\chi_\rho|g|\chi_\nu\chi_\sigma >$

$[\mathrm{K}(\mathrm{R})]_{\mu\nu} = \sum_{\rho\sigma}(\mathrm{R})_{\sigma\rho} < \chi_\mu\chi_\rho|g|\chi_\sigma\chi_\nu >$

Only two-electron integrals involving sums over all the possible values of the quantum number m for an atomic function characterized by given values of n and l are necessary.

We use gaussian-type basis functions $Y_{lm}exp(-\alpha r^2)$, Y_{lm} being a linear combination of terms of the form $x^{n_x}y^{n_y}z^{n_z}$ giving the correct angular part of the wavefunction. Introducing a parameter α a typical two-electron integral can be written as:

$$\lim_{\alpha\to 0}\int exp(-\alpha(\mathrm{r}_1.\mathrm{r}_2))exp(-\alpha_1(\mathrm{r}_1)^2)exp(-\alpha_2(\mathrm{r}_2)^2)/r_{12}d\mathrm{r}_1d\mathrm{r}_2 \qquad (1)$$

where $r_{12} = |\mathrm{r}_1 - \mathrm{r}_2|$;

$\alpha_1 = \alpha_i + \alpha_j$; $\alpha_2 = \alpha_k + \alpha_l$ for $< \chi_i\chi_k|g|\chi_j\chi_l >$ (coulomb integral, J)

$\alpha_1 = \alpha_i + \alpha_l$; $\alpha_2 = \alpha_k + \alpha_j$ for $< \chi_i\chi_k|g|\chi_l\chi_j >$ (exchange integral, K)

The basic integral in (1), namely,

$$\int exp(-\alpha(\mathrm{r}_1.\mathrm{r}_2))exp(-\alpha_1(\mathrm{r}_1)^2)exp(-\alpha_2(\mathrm{r}_2)^2)/r_{12}d\mathrm{r}_1d\mathrm{r}_2 \qquad (2)$$

is a very simple function of α, α_1 and α_2. We obtain the whole two-electron integral,

for any orbital types, simply by applying repeatedly the operator $\delta/\delta\alpha'$, $\alpha' = \alpha$ or α_1 or α_2 to equation (2).

For s and p type functions, for example, integrals are calculated by the following formulae, which refer to the sums over all orbitals within each quantum shell

$$J(ss) = K(ss) = 2\pi^{5/2}/[\alpha_1\alpha_2(\alpha_1+\alpha_2)^{1/2}]$$

$$J(sp) = \pi^{5/2}[2(\alpha_1)^2 + 3\alpha_1\alpha_2]/[(\alpha_1\alpha_2)^2(\alpha_1+\alpha_2)^{3/2}]$$

$$K(sp) = \pi^{5/2}/[\alpha_1\alpha_2(\alpha_1+\alpha_2)^{3/2}]$$

$$J(pp) = 3/2\pi^{5/2}[2(\alpha_1)^2 + 2(\alpha_2)^2 + 5\alpha_1\alpha_2]/[(\alpha_1\alpha_2)^2(\alpha_1+\alpha_2)^{5/2}]$$

$$K(pp) = \pi^{5/2}[2(\alpha_1)^2 + 2(\alpha_2)^2 + 7\alpha_1\alpha_2]/[2(\alpha_1\alpha_2)^2(\alpha_1+\alpha_2)^{5/2}]$$

We now define the optimum orbitals as those which yield stationary values of E_{av}, subject to the ausiliary condition which characterize the projection operator properties of the R-matrices (in a non-orthogonal basis)

$$\mathbf{R}_K^\dagger \mathbf{S}\mathbf{R}_K = \mathbf{R}_K \quad ; \mathbf{R}_K^\dagger \mathbf{S}\mathbf{R}_L = 0 \quad ; \sum_K \mathbf{R}_K = \mathbf{1}.$$

The optimum orbitals must satisfy the commutation conditions

$$\bar{\mathbf{h}}\mathbf{R}_K - \mathbf{R}_K\bar{\mathbf{h}} = 0$$

where $\bar{\mathbf{h}} = \sum_K a_K \mathbf{R}_{KZ}\mathbf{h}_Z\mathbf{R}_{KZ} + \sum_{K<L} b_{KL}\mathbf{R}_{KL}\mathbf{h}_{KL}\mathbf{R}_{KL}$

$$\mathbf{R}_{KL} = \mathbf{R}_K + \mathbf{R}_L; \qquad \mathbf{h}_{KL} = \nu_K\mathbf{h}_K - \nu_L\mathbf{h}_L;$$

a_K and b_{KL} are arbitrary parameters. A good convergence is obtained on choosing: $a_K = 1/N_S$, N_S=number of shells; $b_{KL} = 1/[N_S(\nu_K - \nu_L)]$.

The optimum orbitals are therefore calculated solving the equation

$$\bar{\mathbf{h}}\mathbf{C} = \epsilon\mathbf{S}\mathbf{C}$$

For the two-shell system, $\mathbf{h}$ takes the form

$$\mathbf{h} = a_1 \mathbf{R}'_2 \mathbf{h}_1 \mathbf{R}'_2 + a_2 \mathbf{R}'_1 \mathbf{h}_2 \mathbf{R}'_1 + b_{12} \mathbf{R}'_3 \mathbf{h}_{12} \mathbf{R}'_3 \qquad \mathbf{R}'_K = \mathbf{1} - \mathbf{R}_K$$

By this method atomic orbitals can easily be optimized for any given electronic configuration. For group wavefunctions, in which the valence electrons are described using hybrid orbitals, it is clearly important to optimize orbital parameters for an appropriate valence state. Much work remains to be done on the choice of more extended basis sets.

APPENDIX C.

```
C*************************************************************************C
C
C program GROUPWFS performs
C GROUND STATE ENERGIES
C AND DENSITY MATRIX CALCULATIONS
C FOR MOLECULES
C USING THE GROUP FUNCTION APPROACH
C (MMQM - RoyMcWeeny [7])
C CONSIDERING BONDS AND LONE PAIRS
C AS TWO-ELECTRON GROUPS
C (M.Klessinger and R.McWeeny [93])
C
C*************************************************************************C
C
C input data for GROUPWFS are prepared by the program DATGRWFS,
C which receives the following input data:
C
C title (A80)
C output filename (A8), where information on the basis set is written;
C          it must be renamed SOURCE.DAT just before running GROUPWFS
C charge, multiplicity (integer numbers, in free format)
C Z-MATRIX, an input row in free format for each center i, consisting of
C chemical element (A4) (the following are possible at the moment: H,Li,C,N,O,F,Cl)
C nuclear charge
C atom j, connected with j
C bond length
C atom k, such that i-j-k is the bond angle
C bond angle
C atom l, for the definition of the dihedral angle
C dihedral angle
C
C*************************************************************************C
C an output file from DATGRWFS contains the following data
C max, crit, real numbers
C          max is the maximum number of iteration admitted
```

```
C          crit is chosen so that convergence in the GF SCF process is reached
C          when |R^S(i,j) - R_0^S(i,j)| < crit for every i,j
C            where R^S and R_0^S are the density matrices for group S in two subsequently cycles
norb, nco, integer numbers,
C            norb is the total number of orbitals,
C            nco is the number of core orbitals
C nic(i), i=1,nco, defines which orbitals are core orbitals
C nrv(i), i=1,norb, defines which orbitals are valence orbitals
C natoms, nbond, are the numbers of atoms and groups respectively
C elm(i), iznuc(i), x(i), y(i), z(i), one row for each centre i
C nbonat(1,i), i=1,nbond
C nbonat(2,i), i=1,nbond
C nbonat defines groups
C >>>>>>>>>>>>>>>>>>>>
C
      subroutine heffgr(norb,ss,hh)
      implicit real*8(a-h,o-z)
      dimension ss1(30,30),hh1(30,30),g1(465,465)
      dimension ss(norb,norb),hh(norb,norb)
      dimension gg(108445)
C with 30 basis function, 108445 two-electron must be calculated
C in general nn2=[n2(n2+1)]/2, where n2=[norb(norb+1)]/2
C two-electron integrals are needed
C
C >>>> from a previous calculation of the integrals on the
C >>>> AO basis the matrices ss and hh are received
C >>>> containing overlap and hamiltonian integrals respectively
C >>>> two electron integrals are read and stored in gg
C
                                        .....
      nval=norb-nco
      n2v=nval*(nval+1)/2
      call hefforg(nco,norb,nn2,ss,hh, gg,nval,n2v,ss1,hh1,g1,max,crit)
      stop
      end
c*
      subroutine hefforg(nco,norb,nn2,ss,hh,gg,nval,n2v, ss1,hh1,g1,max,crit)
      implicit real*8(a-h,o-z)
      dimension ss(norb,norb),hh(norb,norb),gg(nn2)
      dimension ss1(nval,nval),hh1(nval,nval),g1(n2v,n2v)
      common/heff/hg(49,3,3),grs(49,49,3,3,3,3),gur(49,3,3)
      common/gs/gjk(49,3,3)
      dimension rr(49,3,3),en1(3),cr(49,3,3),nic(5),nrv(30)
      common/p12/p1(3,3,2,2),p2(6,3,3)
```

```
.....
      common/co/x(30),y(30),z(30),iznuc(30)
 >>>> now input data are read
.....
      call pp
C the subroutine pp prepares matrices P1 and P2
C for taking into account spin integration for chosed shell systems
C >>>> P1 and P2 are formal transition density matrices
C >>>> among the MOs of the basis
C
C >>>> in subroutine dbarra core energy ecor and nuclear energy enuc are computed and
C >>>> Schmidt ortogonalization and an integrals tranformation are performed;
C >>>> the resulting integrals (stored in ss1, hh1, g1) are on a basis of
C >>>> localized MOs, in the order:
C >>>> nleg bonding orbitals one for each bond (two for double bonds),
C >>>> nleg anti-bonding orbitals one for each bond (two for double bonds),
C >>>> nlp lone pair orbitals, such that nbond=nleg+nlp;
C >>>> moreover, by default, penetrative epen and exchange exch corrections
C >>>> for non-orthogonality are calculated
C >>>> (or, alternatively, Lowdin orthoginalization is performed, if nopt=1)
C
      call dbarra(nval,nleg,enuc,norb,nco,nn2,nic,nrv,ss,hh,gg,n2v,
     * ...,ecor,epen,exch,ss1,hh1,g1,nopt)
C >>>> subroutine rgroup fills up common/heff/ and common/gs/ with integrals
C >>>> stored in an appropriate form for subsequent use in the
C >>>> subroutine hefch4, where GF SCF procedure is performed
C
      call rgroup(nleg,nval,n2v,ss1,hh1,g1)
      call hefch4(nleg,max,crit,rr,cr)
114   format(3f20.8)
      do 46 i=1,nleg
      write(6,*)' cr',i
      do 46 j=1,3
      write(6,114)(cr(i,j,k),k=1,3)
46    continue
      do 47 i=1,nleg
      write(6,*)
      write(6,*)' dens. mat.',i
      do 47 j=1,3
      write(6,114)(rr(i,j,jj),jj=1,3)
47    continue
      do 30 ir=1,nleg
      do 50 j=1,3
      en1(j)=zero
```

```
      do 50 k=1,3
      en1(j)=en1(j)+cr(ir,k,1)*(hg(ir,k,j)+(gjk(ir,k,j)
     * +gur(ir,k,j))/two)
50     continue
      enr=zero
      do 40 k=1,3
40     enr=enr+en1(k)*cr(ir,k,1)
      write(6,*)'gr.R=',ir,'En(R)=',enr
30     eval=eval+enr
      nlp=nval-nleg*2
      do 35 ju=1,nlp
      jnu=ju+nleg*2
      muu=lab(jnu,jnu)
      hju=hh1(jnu,jnu)*2+g1(muu,muu)
      do 37 jv=1,nlp
      if(jv.eq.ju)goto 37
      jnv=jv+nleg*2
      muv=lab(jnu,jnv)
      mvv=lab(jnv,jnv)
      hju=hju+two*(g1(muu,mvv)-.5d0*g1(muv,muv))
37     continue
      do 42 is=1,nleg
      isv=is+nleg
      ms1s1=lab(is,is)
      ms1s2=lab(is,isv)
      ms2s2=lab(isv,isv)
      mus1=lab(is,jnu)
      mus2=lab(isv,jnu)
      do 42 mu=1,3
      do 42 nu=1,3
      aaa=p1(mu,nu,1,1)*(g1(ms1s1,muu)-g1(mus1,mus1)/two)+
     * (p1(mu,nu,1,2)+p1(mu,nu,2,1))*
     * (g1(ms1s2,muu)-g1(mus1,mus2)/two)+
     * p1(mu,nu,2,2)*(g1(ms2s2,muu)-g1(mus2,mus2)/two)
      hju=hju+aaa*cr(is,mu,1)*cr(is,nu,1)
42     continue
      eval=eval+hju
35     continue
      energy=ecor+eval+enuc
      write(6,*)
      write(6,*)
      write(6,*)'E(APSG)=',energy
      if(nopt.eq.0)write(6,*)'E(tot)=',energy+exch+epen
      return
```

```
      end
      subroutine rgroup(nleg,nval,n2v,ss,hh,g)
      implicit real*8(a-h,o-z)
      common/heff/hg(49,3,3),grs(49,49,3,3,3,3),gur(49,3,3)
      common/p12/p1(3,3,2,2),p2(6,3,3)
      COMMON/BOND/nbonat(2,30)
      dimension gu(49,2,2)
      dimension ss(nval,nval),hh(nval,nval),g(n2v,n2v)
      dimension hr(49,2,2),gr(49,3,3),gserv(49,49,3,3,2,2)
      data zero,two/0.0d0,2.0d0/
      mi=6
      nlp=nval-nleg*2
      do 10 j=1,nleg
      jj=j+nleg
      mab=lab(j,jj)
      mbb=lab(jj,jj)
      maa=lab(j,j)
      hr(j,2,1)=hh(jj,j)
      hr(j,1,2)=hh(j,jj)
      hr(j,1,1)=hh(j,j)
      hr(j,2,2)=hh(jj,jj)
      gu(j,2,1)=zero
      gu(j,1,2)=zero
      gu(j,1,1)=zero
      gu(j,2,2)=zero
      do 15 ju=1,nlp
      jnu=ju+nleg*2
      mau=lab(j,jnu)
      mbu=lab(jj,jnu)
      muu=lab(jnu,jnu)
      gu(j,2,1)=gu(j,2,1)+two*g(mab,muu)-g(mau,mbu)
      gu(j,1,2)=gu(j,1,2)+two*g(mab,muu)-g(mau,mbu)
      gu(j,1,1)=gu(j,1,1)+two*g(maa,muu)-g(mau,mau)
      gu(j,2,2)=gu(j,2,2)+two*g(mbb,muu)-g(mbu,mbu)
15    continue
      gr(j,1,1)=g(maa,maa)
      gr(j,2,1)=g(mab,maa)
      gr(j,1,2)=g(maa,mab)
      gr(j,2,2)=g(mab,mab)
      gr(j,3,1)=g(mbb,maa)
      gr(j,1,3)=g(maa,mbb)
      gr(j,3,2)=g(mbb,mab)
      gr(j,2,3)=g(mab,mbb)
      gr(j,3,3)=g(mbb,mbb)
```

```
      do 10 nl=1,nleg
      if(nl.eq.j)goto10
      jnl=nleg+nl
      mad=lab(j,jnl)
      mcc=lab(nl,nl)
      mbc=lab(nl,jj)
      mdd=lab(jnl,jnl)
      mac=lab(j,nl)
      mcd=lab(nl,jnl)
      mbd=lab(jj,jnl)
      do 20 mu=1,3
      do 20 nu=1,3
      gserv(j,nl,mu,nu,1,1)=(g(maa,mcc)-g(mac,mac)/two)*p1(mu,nu,1,1)
     * +(g(mab,mcc)-g(mbc,mac)/two)*(p1(mu,nu,2,1)+p1(mu,nu,1,2))
     * +(g(mbb,mcc)-g(mbc,mbc)/two)*p1(mu,nu,2,2)
      gserv(j,nl,mu,nu,1,2)=(g(maa,mcd)-g(mac,mad)/two)*p1(mu,nu,1,1)
     * +(g(mab,mcd)-g(mad,mbc)/two)*p1(mu,nu,2,1)
     * +(g(mab,mcd)-g(mac,mbd)/two)*p1(mu,nu,1,2)
     * +(g(mbb,mcd)-g(mbc,mbd)/two)*p1(mu,nu,2,2)
      gserv(j,nl,mu,nu,2,1)=(g(maa,mcd)-g(mad,mac)/two)*p1(mu,nu,1,1)
     * +(g(mab,mcd)-g(mbd,mac)/two)*p1(mu,nu,2,1)
     * +(g(mab,mcd)-g(mbc,mad)/two)*p1(mu,nu,1,2)
     * +(g(mbb,mcd)-g(mbc,mbd)/two)*p1(mu,nu,2,2)
      gserv(j,nl,mu,nu,2,2)=(g(maa,mdd)-g(mad,mad)/two)*p1(mu,nu,1,1)
     * +(g(mab,mdd)-g(mad,mbd)/two)*(p1(mu,nu,2,1)+p1(mu,nu,1,2))
     * +(g(mbb,mdd)-g(mbd,mbd)/two)*p1(mu,nu,2,2)
20    continue
10    continue
      do 70 mu=1,3
      do 70 nu=1,3
      do 70 k=1,3
      do 70 l=1,3
      do 70 j=1,nleg
      do 70 nl=1,nleg
      if(j.eq.nl)goto70
      grs(j,nl,mu,nu,k,l)=zero
      do 60 ia=1,2
      do 60 ib=1,2
      grs(j,nl,mu,nu,k,l)=grs(j,nl,mu,nu,k,l)+
     * gserv(j,nl,mu,nu,ia,ib)*p1(k,l,ib,ia)
60    continue
70    continue
      do 30 j=1,nleg
      do 30 mu=1,3
```

```
      do 30 nu=1,mu
      isl=lab(mu,nu)
      hg(j,mu,nu)=zero
      gur(j,mu,nu)=zero
      do 40 k=1,2
      do 40 l=1,2
      hg(j,mu,nu)=hg(j,mu,nu)+hr(j,k,l)*p1(nu,mu,l,k)
40    gur(j,mu,nu)=gur(j,mu,nu)+gu(j,k,l)*p1(nu,mu,l,k)
      if(mu.ne.nu)gur(j,nu,mu)=gur(j,mu,nu)
      do 50 k=1,3
      do 50 l=1,3
50    hg(j,mu,nu)=hg(j,mu,nu)+gr(j,k,l)*p2(isl,l,k)/two
      if(mu.ne.nu) then
      hg(j,nu,mu)=hg(j,mu,nu)
      end if
30    continue
      return
      end
c*
      subroutine pp
      implicit real*8(a-h,o-z)
      common/p12/p1(3,3,2,2),p2(6,3,3)
      data zero,one,two/0.0d0,1.0d0,2.0d0/
      sq2=dsqrt(two)
      do 10 i=1,3
      do 10 ii=1,3
      do 10 j=1,2
      do 10 k=1,2
      p1(i,ii,j,k)=zero
10    continue
      do 20 i=1,6
      do 20 j=1,3
      do 20 k=1,3
      p2(i,j,k)=zero
20    continue
      p1(1,1,1,1)=two
      p1(2,1,2,1)=sq2
      p1(1,2,1,2)=sq2
      p1(2,2,1,1)=one
      p1(2,2,2,2)=one
      p1(3,2,2,1)=sq2
      p1(2,3,1,2)=sq2
      p1(3,3,2,2)=two
      p2(1,1,1)=two
```

```
      p2(2,1,2)=sq2
      p2(2,2,1)=sq2
      p2(3,1,3)=one
      p2(3,2,2)=two
      p2(3,3,1)=one
      p2(4,2,2)=two
      p2(5,2,3)=sq2
      p2(5,3,2)=sq2
      p2(6,3,3)=two
      return
      end
      subroutine buildhef(nleg,jr,rr,hef)
      implicit real*8(a-h,o-z)
      common/p12/p1(3,3,2,2),p2(6,3,3)
      common/heff/hg(49,3,3),grs(49,49,3,3,3,3),
     * gur(49,3,3)
      common/gs/gjk(49,3,3)
      dimension hef(3,3),rr(49,3,3)
      data zero/0.0d0/
      do 10 mu=1,3
      do 10 nu=1,mu
      gjk(jr,mu,nu)=zero
      do 20 js=1,nleg
      if(js.eq.jr)goto 20
      do 50 k=1,3
      do 50 l=1,3
      gjk(jr,mu,nu)=gjk(jr,mu,nu)+rr(js,k,l)*grs(jr,js,nu,mu,k,l)
50    continue
20    continue
      hef(mu,nu)=gjk(jr,mu,nu)+hg(jr,mu,nu)+gur(jr,mu,nu)
      hef(nu,mu)=hef(mu,nu)
      gjk(jr,nu,mu)=gjk(jr,mu,nu)
10    continue
      return
      end
c*
      subroutine hefch4(nleg,max,crit,rr,cr)
      implicit real*8(a-h,o-z)
      dimension rr0(49,3,3),rr(49,3,3),hef(3,3),r(3,3),r0(3,3)
      dimension u(3,3),e(3),num(49),cr(49,3,3)
      data zero,one,two/0.0d0,1.0d0,2.0d0/
      m=3
      ncyc=0
      ig=1
```

```
      do 10 i=1,m
      do 10 j=1,m
      do 20 k=1,nleg
      rr0(k,i,j)=zero
20    rr(k,i,j)=zero
      r0(i,j)=zero
10    continue
      do 15 k=1,nleg
      rr(k,1,1)=two
15    num(k)=1
      do 18 i=1,m
      do 18 j=1,m
18    r(i,j)=rr(1,i,j)
      write(6,3)
3     format(/,2x,'eigenvalues:')
12    call buildhef(nleg,ig,rr,hef)
      call diag(hef,u,e,m)
      do 30 i=1,m
30    e(i)=hef(i,i)
      write(6,4)(e(i),i=1,m)
4     format(3(2x,f18.10))
      call ord(hef,u,e,m)
      do 40 i=1,m
      do 40 j=1,m
      rr(ig,i,j)=u(i,1)*u(j,1)
      r(i,j)=rr(ig,i,j)
      cr(ig,i,j)=u(i,j)
40    continue
      call test(m,r,r0,crit,num(ig))
      do 60 i=1,m
      do 60 j=1,m
      rr0(ig,i,j)=rr(ig,i,j)
60    continue
      if(num(ig))32,32,33
32    do 70 ir=1,nleg
      if(num(ir))70,70,33
70    continue
      write(6,1)ncyc
1     format(/,2x,i3,' CYCLES',/)
      goto201
34    write (6,2)max
2     format(1x,'not converged ',i3,' cycles',/)
      goto 201
33    if(ig.eq.nleg)goto 36
```

```
      ig=ig+1
      goto 42
36    if(max-ncyc)34,34,35
35    ig=1
      ncyc=ncyc+1
42    do 80 i=1,m
      do 80 j=1,m
80    r0(i,j)=rr0(ig,i,j)
      goto 12
201   return
      end
```

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